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Surface tensions of some binary fused salt systems

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Abstract

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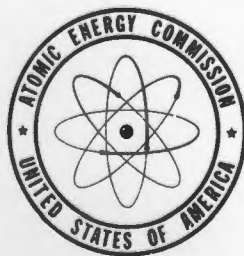
UNITED STATES ATOMIC ENERGY COMMISSION

**SURFACE TENSIONS OF SOME BINARY
FUSED SALT SYSTEMS**

By
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June 1957

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Ames, Iowa



Technical Information Service Extension, Oak Ridge, Tenn.

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TABLE OF CONTENTS

| | Page |
|--|------|
| ABSTRACT | 4 |
| INTRODUCTION | 7 |
| EXPERIMENTAL INVESTIGATION | 13 |
| Choice of Method | 13 |
| The Apparatus | 17 |
| The capillary | 17 |
| The supply of inert gas | 22 |
| The manometer | 24 |
| The means of controlling and measuring the temperature | 25 |
| Procedure | 27 |
| Preparation and analysis of the melts | 27 |
| Measurement of the surface tension | 29 |
| RESULTS | 33 |
| DISCUSSION | 47 |
| Pure Fused Salts | 47 |
| Binary Mixtures | 51 |
| Evaluation of the Maximum Bubble Pressure Method | 72 |
| Analysis of Errors | 74 |
| BIBLIOGRAPHY | 78 |

ABSTRACT

The surface tensions of eight pure fused salts-- NaNO_3 , KNO_3 , AgNO_3 , LiCl , NaCl , PbCl_2 , KCl and ZnCl_2 --and nine binary mixtures-- NaNO_3 - KNO_3 , AgNO_3 - NaNO_3 , AgNO_3 - KNO_3 , NaCl - KCl , PbCl_2 - LiCl , PbCl_2 - NaCl , PbCl_2 - KCl , PbCl_2 - RbCl , and PbCl_2 - CsCl --were measured by the maximum bubble pressure method. Surface tension showed essentially linear variation with temperature in all cases.

As would be expected, large differences were found between the surface tensions of the pure fused salts. The higher surface tension of molten AgNO_3 compared to NaNO_3 was explained in terms of differences in the polarizability of the metal ions in the melts. The low surface tension of ZnCl_2 was assumed to result from extensive association in this melt.

The surface tension isotherms of the systems NaNO_3 - KNO_3 and NaCl - KCl were found to exhibit small negative deviations from ideality. The greater negative deviations from ideality which were found in the systems AgNO_3 - NaNO_3 and AgNO_3 - KNO_3 were attributed to polarizability differences between the metal ions. The limited data suggested that in binary mixtures of fused salts with a common anion, the deviations of the surface tension isotherms from ideality increase as the differences between the sizes of the replacing cations increase.

Actual minima were observed in the surface tension isotherms of the systems $\text{PbCl}_2\text{-KCl}$, $\text{PbCl}_2\text{-RbCl}$, and $\text{PbCl}_2\text{-CsCl}$; no minima were observed in the systems $\text{PbCl}_2\text{-LiCl}$ and $\text{PbCl}_2\text{-NaCl}$. These minima were attributed to the presence of complex ions or other surface active aggregates in these melts. Other physical measurements strongly support the existence of complex ions, very likely anionic complexes of lead, in the system $\text{PbCl}_2\text{-KCl}$.

The trend in the character of the PbCl_2 -alkali metal chloride surface tension isotherms was shown to be in accord with the fact that any anionic complexes in these melts would be more stable in the presence of large cations with low polarizing power than in the presence of small ions with large polarizing power.

Further evidence for complexing in the PbCl_2 -alkali metal chloride melts was the presence of a yellow color in those melts whose surface tension isotherms exhibited minima; no yellow color was observed in the $\text{PbCl}_2\text{-LiCl}$ and $\text{PbCl}_2\text{-NaCl}$ systems. This yellow color which persisted in the solid state at high temperatures was found to increase in intensity with increase in the size of the alkali metal ion.

It was pointed out that there is no reason to assume that the complexing in these melts consists only of discrete ions. It was proposed that there are also local aggregations of ions whose structures resemble the structure of the solid state.

Surface Tensions of Some Binary Fused Salt Systems*

June L. Dahl and F. R. Duke

INTRODUCTION

The increasing technological importance of high temperature processes has emphasized the need for specific data concerning the physical and chemical properties of fused salt systems. Aside from their practical significance, such data should be of great value in the study of the liquid state; for example, they should aid in the development of more adequate theories of concentrated aqueous solutions than exist at present.

There is no direct way to determine the structures of fused salts. Some X-ray diffraction studies of molten salts have been carried out (1-7), and from the resulting data nearest neighbor relationships in various pure salts have been determined. However, the interpretation of the diffraction patterns given by liquids composed of complex molecules is quite difficult, and in most cases little direct information about an unknown structure is obtained. In general, one can say only that a certain assumed structure and arrangement is not inconsistent with the observed diffraction data.

It will be necessary to amass a considerable amount of physico-chemical data relating to the various properties of fused salts--e.g., densities, conductivities, viscosities, transference numbers, and activities--before it will be possible to formulate a really precise description of the nature

*This report is based on a Ph.D. thesis by June L. Dahl submitted June, 1957, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

of these liquids. A study of the surface tensions of fused salts and their mixtures should be expected to aid in such a formulation.

Since the molecules in the surface of a liquid are subject to a strong attraction toward the bulk of the liquid, the surface will contract until its area is the smallest possible for a given volume. Work must therefore be done to increase the surface area, that is, to bring molecules from the interior to the surface against the cohesive forces in the liquid. Surface tension is a measure of this work. The work done in extending a surface which possesses a tension of γ dynes/cm by 1 cm² will be γ ergs/cm². The free surface energy of such a surface will be γ ergs/cm².

It would seem that comparison of the surface tensions of various fused salts should give some indication of the type and relative magnitude of the interactions between the species in the melts. Surface tensions of mixtures of fused salts should be especially informative, since the formation of complex ions or other surface-active species should cause large negative deviations of the surface tension-composition isotherms from ideality. Any complex ions formed would have smaller residual electrical fields of force than simple ions in the melts and would thus tend to concentrate in the surface. This would result in a lowering of the surface tension from

the value it would have if the interactions between the ions were the same as they are in the pure salts.

Jaeger (8,9) was the first to make accurate measurements of the surface tensions of fused salts. He perfected the maximum bubble pressure method for use over the temperature range from -80°C to 1650°C . He used it to measure the surface tensions of some fifty molten salts including the halides, nitrates, metaborates, metasilicates, sulphates, molybdates, and tungstates of the alkali metals and such compounds as S_2Cl_2 , PCl_3 , PI_3 , AsCl_3 , AsBr_3 , SbCl_3 , BiCl_3 , and BiBr_3 . As would be expected, he noted marked differences between the surface tensions of the salts of the alkali metals and the latter group of compounds. He found that at constant temperature the surface tensions of the alkali halides decrease with increasing atomic weight of the alkali metal and also with increasing atomic weight of the halogen. This is the reverse of the situation for such compounds as PCl_3 , AsCl_3 , and SbCl_3 ; in these cases the surface tensions increase as the atomic weight increases. However, Jaeger did observe that the surface tensions of all the substances studied decreased with increasing temperature; in fact the surface tension-temperature curves were nearly linear in all cases.

Semenchenko and Shikhobalova (10-12) have published data on the surface tensions of several mixtures of fused salts. They were initially interested in correlating changes in

surface tension with changes in particle size of the solids crystallized from those melts whose surface tensions were measured. They felt that admixtures which lowered the surface tension of a melt should lower the particle size, and indeed this was found to be the case. Their work by no means proved, however, that surface tension was the only factor affecting the size of the crystals obtained in their experiments. They also studied the surface tensions of mixtures of Li_2SO_4 and Na_2SO_4 with NaCl , KCl , RbCl , and CsCl . The system BaCl_2 - K_2SO_4 exhibited a minimum in surface tension at 50 mole per cent; this minimum was attributed to the formation of BaSO_4 molecules in the melt.

Barzahovskii (13) studied the systems CaCl_2 - NaCl , BaCl_2 - NaCl , KCl - NaCl , and PbCl_2 - NaCl . The surface tensions of the first three systems were nearly additive with only small negative deviations from additivity. The data for the PbCl_2 - NaCl system indicated a distinct minimum at about 75 mole per cent PbCl_2 .

The surface tensions of the quaternary system NaCl - KCl - CaCl_2 - MgCl_2 (14) and the system BaCl_2 - KCl (15) have been studied. Small negative deviations from additivity were observed for these systems.

Boardman, Palmer, and Heymann (16) used the maximum bubble pressure method to measure the surface tensions of several binary mixtures of fused salts. Large negative

deviations were observed for the systems $\text{CdCl}_2\text{-KCl}$ and $\text{PbCl}_2\text{-KCl}$; the surface tension isotherms actually exhibited minima. These deviations from ideality were attributed to the formation of the complex ions CdCl_3^- and PbCl_3^- in the melts. Large negative deviations were observed for the systems AgCl-PbCl_2 , AgCl-KCl , and AgBr-KBr , but the authors were hesitant to ascribe these effects to complex ion formation and instead attributed them to "coordination of silver and halide ions on mixing". The system $\text{CdCl}_2\text{-PbCl}_2$ was unique in that it showed positive deviations from ideality. Boardman, Palmer, and Heymann explained these deviations in the following way. Pure CdCl_2 is assumed to be partially associated or polymerized in the molten state. This conclusion is consistent with their observation that the surface tension of pure CdCl_2 is much lower than that of CaCl_2 , despite the fact that both cations have approximately the same ionic radius. The addition of PbCl_2 to a CdCl_2 melt is assumed to cause dissociation of the CdCl_2 polymers, thereby increasing the ionic character of the melt with a resultant positive deviation of the surface tension-composition isotherms from ideality.

The present research was begun in an effort to obtain additional fundamental information on fused salt systems. The systems $\text{AgNO}_3\text{-NaNO}_3$ and $\text{AgNO}_3\text{-KNO}_3$ were investigated to supplement transference measurements being carried out in this laboratory (17, 18).

Many studies have been made to determine the possibility of complex ion formation in the molten state. There is a large amount of evidence supporting the existence of complex ions in the PbCl_2 -KCl system. Molar volumes (19), conductivities (20), and transference studies (21) all appear to substantiate their existence. In solids and in aqueous solutions the stability of a complex ion depends on its environment. It would appear significant to study the stability of these lead chloride complex ions as a function of their environment--in this case, the alkali metal ion in the melt. Thus a study of the surface tensions of the PbCl_2 -alkali metal chloride systems was undertaken.

EXPERIMENTAL INVESTIGATION

Choice of Method

Adam (22) and Harkins (23) give excellent reviews of the various methods available for measuring surface tension. Unfortunately, most of them are not satisfactory for use with corrosive materials at high temperatures. As Harkins (23) points out, there is no single best method for measuring surface tension. Various factors must be taken into consideration when choosing a method to use for a particular liquid or group of liquids. The most important factors to be considered when selecting a method to use for measuring the surface tensions of fused salts are listed below:

1. The method should be on a firm theoretical basis so that it will be possible to calculate accurate absolute surface tensions.
2. Only a small portion of the apparatus involved should come in contact with the melt, as it is practically impossible to find any material which is completely resistant to the corrosive action of fused salts.
3. It should be necessary to maintain temperature uniformity over only a small portion of the apparatus, as it is difficult to completely eliminate thermal gradients at high temperatures.

4. The method should involve as little handling of the melt as possible.
5. No visual observations of the melt should be required.
6. The accuracy and precision of the results should be as great at the highest as at the lowest temperatures.

The four most common methods of measuring surface tension are capillary rise, drop weight, ring method, and maximum bubble pressure method. Of these only the maximum bubble pressure method satisfies the criteria listed above.

The method of capillary rise has seen limited application (24, 25), but it is not well suited to the determination of the surface tensions of fused salts. Capillaries are badly corroded even by low melting salts, and in addition temperature uniformity is very difficult to maintain over the length of the tube.

The experimental difficulties involved in the drop weight method are too great to make it practical to use this method.

Methods involving the measurement of the force required to detach a body from the surface of a liquid are applicable, although they do not give results of the highest accuracy. Modifications employing a circular ring of wire or the end of a short thin-walled circular tube are now on a firm theoretical basis. These methods have been used successfully in the study of melts with high viscosities, e.g., condensed phosphates (26), silicates (27), and molten cryolite (28). Their chief

drawback is the difficulty in maintaining a clean surface throughout the course of the measurements; however, their value in work on viscous systems should not be overlooked.

The maximum bubble pressure method which was first suggested by Simon (29) can be adapted to give precise results at high temperatures. It involves the measurement of the maximum pressure developed in a bubble formed at the tip of a capillary immersed in the salt. If the capillary bore were infinitesimally small this maximum pressure would be equal to the pressure necessary to depress a meniscus by an amount equal to the capillary rise. If the capillary were immersed to a depth l in the liquid the maximum pressure in the bubble, P_{\max} , would equal $gl(D - d) + 2\gamma/r$ where γ is the surface tension, r is the radius of the tube, l is the depth of immersion, D is the density of the liquid, d is the density of the gas, and g is the acceleration due to gravity. The quantity $gl(D - d)$ is that portion of the pressure which is necessary to push the liquid down the tube to the depth l below the plane surface of the liquid.

The theory of bubble formation from tubes of finite radii was first discussed by Cantor (30). His equation for the maximum bubble pressure was corrected by Schroedinger (31), who gave the formula:

$$\gamma = \frac{\bar{p}r}{2} \left[1 - \frac{2}{3} \frac{r}{h} - \frac{1}{6} \left(\frac{r}{h} \right)^2 \cdot \cdot \cdot \right]$$

where γ is the surface tension in dynes/cm, r is the radius of the capillary, \bar{p} is the maximum pressure difference inside and outside the bubble at the level of the end of the tip,

$$h = \frac{\bar{p}}{g(D - d)},$$

where g is the acceleration of gravity, D is the density of the liquid, and d is the density of the gas (ordinarily this can be neglected).

Sugden (32) has shown that Schroedinger's approximation is valid for values of $\sqrt{r/h}$ up to 0.2. When $\sqrt{r/h}$ is greater than 0.2 it is necessary to use Sugden's tables and his method of successive approximations. Since $\sqrt{r/h}$ was less than 0.2 in these investigations, Schroedinger's equation was used in all the calculations.

Hoffman (33) and Tripp (34) thoroughly investigated the maximum bubble pressure method. They showed that the mathematical theory is in accord with experiment only if the bubbles are formed slowly. Phenomena are very complex when bubbles are formed rapidly. Once the maximum pressure has been attained in the formation of a bubble, the subsequent decrease in pressure cannot influence the maximum pressure attained in the formation of that bubble, but it can affect the pressure of the next bubble. For this reason the use of a single tube and slow bubble formation is best, although modifications

involving two tubes and a rapid stream of bubbles have been used in measuring the surface tensions of liquids at room temperature (32, 35).

The Apparatus

The measurement of the surface tensions of fused salts by the maximum bubble pressure method involves the very slow formation of a bubble at the tip of a capillary immersed in the salt and the subsequent determination of the maximum pressure in the bubble at the very instant that it bursts. In order to calculate the surface tension from Schroedinger's equation, the radius of the capillary, its depth of immersion in the salt, and the density of the melt at the temperature of the measurement must also be known.

The discussion of the apparatus used to measure the surface tension by the maximum bubble pressure method can conveniently be divided into four categories: (a) the capillary, (b) the supply of inert gas, (c) the manometer, (d) the means of controlling and measuring the temperature.

The capillary

A 90% platinum-10% rhodium capillary was fabricated by the American Platinum Works (Newark, New Jersey). It was five

inches long, 6 mm wide at the upper end and tapered to a 2 mm outside diameter at the tip. A brass rim grooved to accommodate an O-ring was soldered to the top of the capillary. The capillary bore was approximately 0.5 mm at the tip. Prior considerations showed that this bore size would be quite satisfactory; if the bore is larger than 1.0 mm the maximum bubble pressures get very small, whereas a bore diameter smaller than 0.1 mm is difficult to measure with accuracy.

Careful attention must be paid to the capillary tip if accuracy in surface tension measurements by the maximum bubble pressure method is to be obtained. The bore should be as accurately round as possible, the end flat and perpendicular to the axis of the capillary, and the edges very sharp. These requirements were best met by surface grinding the tip to obtain the necessary flat surface, then reaming the hole with a drill bit to obtain the desired circularity. The operations usually had to be repeated several times before the necessary sharpness and circularity were obtained. The tip of the capillary must be checked periodically for wear as even platinum-rhodium alloy is corroded by fused salts. The necessity for proper care and inspection of the capillary cannot be overemphasized.

The diameter of the capillary bore was measured with a Bausch and Lomb microscope using a 24 mm objective and a filar micrometer eyepiece. The capillary was clamped rigidly in a

small V-block with its axis perpendicular to the eyepiece of the microscope. The filar eyepiece was rotated so that measurements were made in several directions and the average of fifty readings was taken as the diameter. The filar eyepiece was calibrated against a Bausch and Lomb stage micrometer which consisted of a scale 1 mm long with divisions spaced at 0.1 mm; the first two 0.1 mm were lined to 0.01 mm.

Accurate measurements of the maximum bubble pressure depend on the capillary being perpendicular to the surface of the melt and its depth of immersion being known. This was accomplished by that portion of the apparatus shown by Figure 1.

Four triangular platforms were supported by three vertical columns of stainless steel pipe. The top platform supported the guide tube C and the pulley A over which passed a cable; a second pulley D connected to one of the vertical columns carried the cable to the winch M. The tube B which slides easily in the guide tube was attached to the cable and to the third platform. This platform and consequently the capillary L which was attached to it were raised and lowered by means of the winch and pulley arrangement. Accurate vertical adjustments of the capillary were made with the micrometer head E. The water jacket H protected the micrometer head from the intense heat of the furnace. The second platform served as a support for the furnace N; a hole was cut in it to allow

Figure 1. Surface tension apparatus

- A Pulley
- B Brass tube
- C Guide tube
- D Pulley
- E Micrometer head
- F To manometer and helium supply
- G Guide wheel
- H Water jacket
- J Water inlet or outlet
- K Shown in detail in Figure 2
- L Capillary
- M Winch
- N Furnace
- P Elevating screw and support

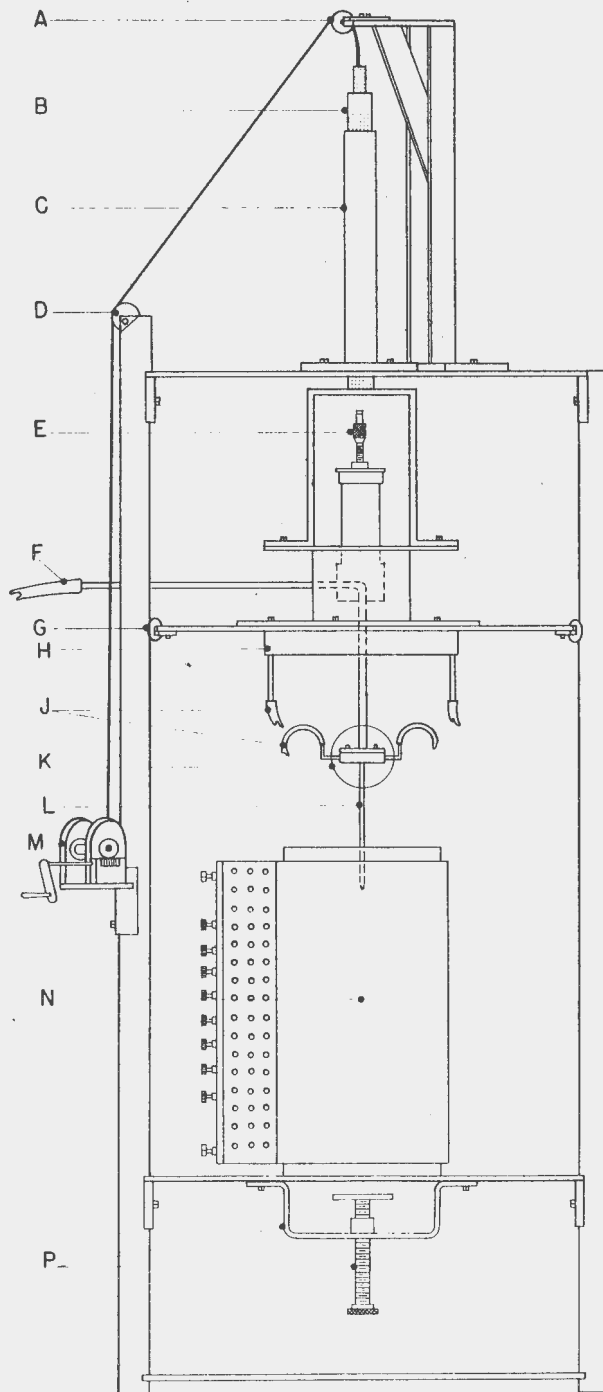
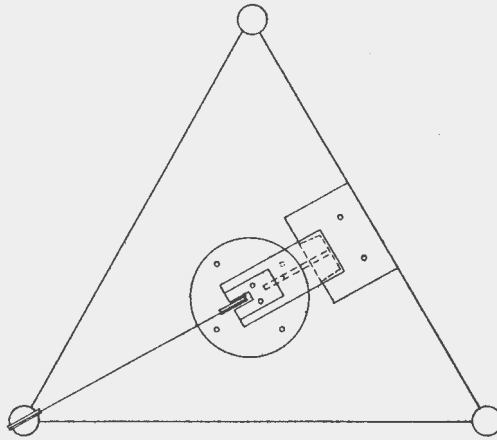


Figure 1

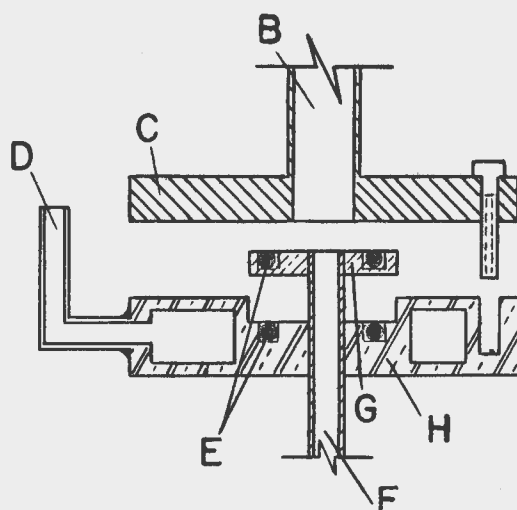
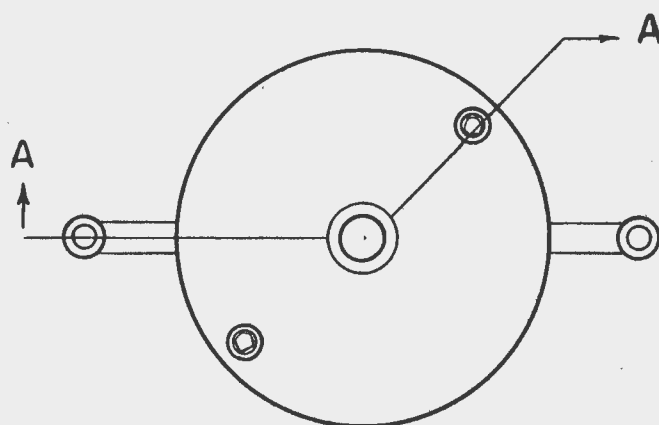
for entrance of the elevating screw P by means of which the crucible could be raised and lowered in the furnace. The bottom platform served merely to increase the rigidity of the frame.

The capillary was joined to the apparatus by means of a pair of flanges C and H as shown in Figure 2. The top flange C was a permanent part of the apparatus shown in Figure 1. The two flanges were screwed tightly together, the two O-rings E assuring an air tight seal. Water was circulated through a cavity in the lower flange H to protect the O-rings from the heat of the furnace and also to keep this portion of the apparatus cool for convenience in handling.

The supply of inert gas

Helium gas of 99.99% purity (The Matheson Co. Inc., Joliet, Illinois) was used to form the bubbles in all the measurements. Any pure inert gas would have been suitable, as differences in the maximum pressures measured with different gases have been shown to be negligible compared with experimental errors. The gas was passed through a drying column packed with ascarite and drierite to remove any possible traces of water and carbon dioxide.

Since bubble formation must be very slow, of the order of one bubble per minute, a sensitive device for controlling the pressure was necessary. A simple needle valve designed



SECTION A A

Figure 2. Arrangement for attaching the capillary to the apparatus

- B To manometer and helium supply
- C Stainless steel flange
- D Water inlet or outlet
- E O-rings
- F Capillary
- G Brass rim
- H Brass flange with cavity

for use in a vacuum system proved most satisfactory, allowing bubble flow to be regulated from one per second to one every three minutes with ease.

Jaeger (8, 9) and Semenchenko and Shikhobalova (10) preheated the gas to the temperature of the measurement in order to prevent undesirable cooling of the surface of the melt during the formation and release of the bubbles from the capillary tip. The author's measurements showed, however, that such precautions were quite unnecessary with the very slow bubble rates involved; no temperature fluctuations were observed during and after the formation of bubbles with non-preheated gas.

The manometer

The manometer was constructed of 20 mm uniform bore tubing. It was enclosed in a glass jacket through which water from a constant temperature bath was circulated by means of a pump. Dibutyl phthalate was chosen as the manometer liquid because of its low volatility and relatively low density. An organic dye, DuPont Oil Red, was added to it to increase the ease with which the menisci could be read. The density of the dibutyl phthalate was measured by the method of hydrostatic weighing; an average of 32 measurements gave a density of $1.0405 \pm 0.0001 \text{ gm/cm}^3$ at $25.0 \pm 0.1^\circ \text{ C}$. Since the same bath

was used to thermostat the manometer and the vessel which held the dibutyl phthalate during the density determinations, temperature errors involved in the conversion of pressure in cm of dibutyl phthalate to pressure in dynes/cm² should be negligible.

The manometer tubes were illuminated by a light source placed above and somewhat in front of the manometer. The manometer was shielded with black paper to cut down glare from other light sources in the room.

The levels of the menisci were estimated to 0.002 cm with a cathetometer (The Gaertner Scientific Corporation, Chicago, Illinois) whose vernier was graduated to 0.005 cm.

The means of controlling and measuring the temperature

The furnace assembly used in this work is shown in Figure 3. The Marshall vertical tube furnace, 13 inches long with a 2 $\frac{1}{2}$ inch inside diameter and 7 inch outside diameter, was provided with a shunt panel having eight binding posts. By placing shunts of appropriate sizes across the binding posts, thermal gradients were reduced to less than 0.5° C over the height of the melt (usually about 2 inches).

The inconel pipe D and stainless steel rod H were inserted inside the furnace core to increase the heat capacity of the system and thus provide greater temperature stability. The

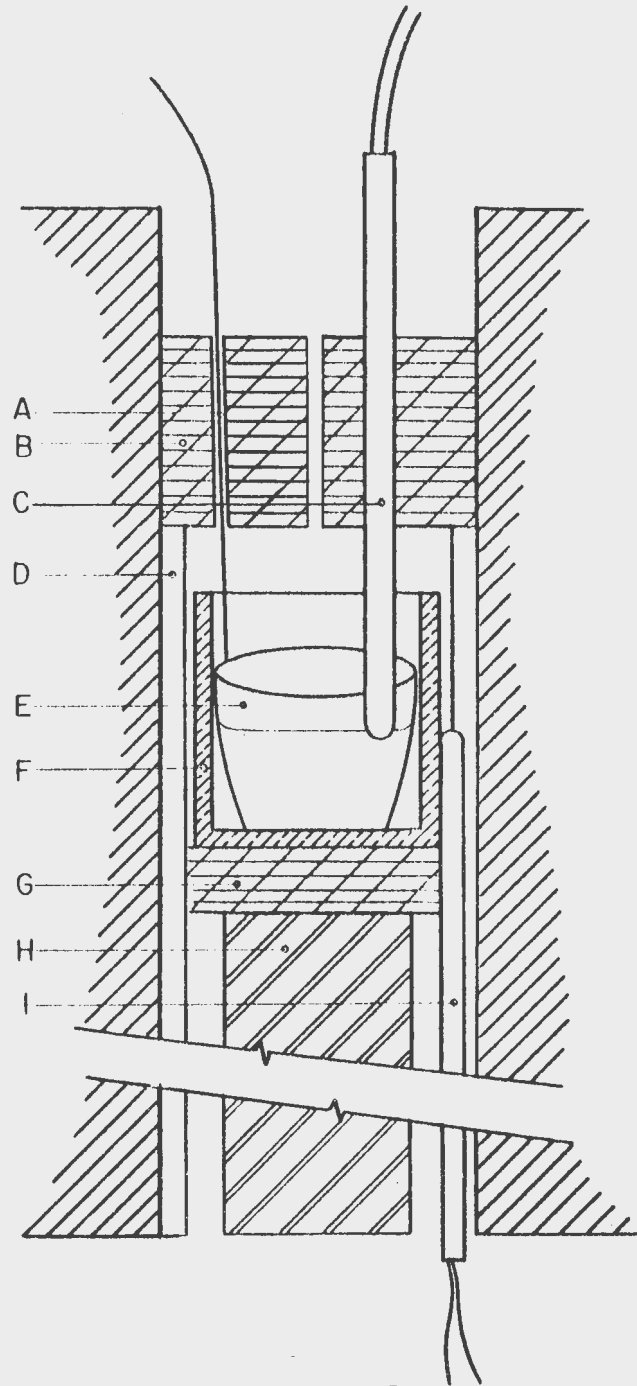


Figure 3. The furnace assembly

- A Platinum wire
- B Transite plug
- C Platinum-platinum 13% rhodium thermocouple
in quartz sheath
- D Inconel pipe
- E Platinum crucible
- F Alundum bucket
- G Transite support
- H Stainless steel rod
- I Chromel-alumel thermocouple in quartz sheath

bottom end of the furnace core was packed with Pyrex wool to cut down heat loss. The melt was contained in a 30 cc platinum crucible E which was placed inside an alundum bucket F to prevent electrical contact between the melt and rest of the system. A platinum wire handle on the alundum bucket allowed samples to be introduced and withdrawn from the furnace easily. The transite plug B, which was provided with three holes to allow entrance for the capillary and measuring thermocouple C and an exit for the platinum wire A, was positioned on top of the inconel pipe.

The temperature was controlled by a Brown Elektronik Indicating Proportioning Controller sensitized by a chromel-alumel thermocouple I. The actual temperature of the melt was measured with a calibrated platinum-platinum, 13% rhodium thermocouple C connected to a Leeds and Northrup potentiometer; emf readings were made to the null point of a sensitive galvanometer.

Procedure

Preparation and analysis of the melts

Baker and Adamson lead chloride and 'Baker Analyzed' Reagent lithium chloride were fused at temperatures just above their melting points, crushed, and stored in a drying oven at

at 110° C. Cesium chloride was obtained from Fischer Scientific Corporation; rubidium chloride from A. D. MacKay Inc.; the lithium chloride, sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, and silver nitrate used were 'Baker Analyzed' Reagent materials. The carefully dried nitrates and alkali chlorides were used without further purification.

The pure lithium chloride melt was prepared in several different ways: (a) fusion in an HCl atmosphere, (b) fusion in a He atmosphere, (c) fusion in the presence of a limited amount of dry air. The surface tension proved to be independent of the method of preparation.

Mixtures were prepared by accurately weighing predetermined amounts of the carefully dried reagents into the platinum crucible which was then placed into the furnace. The temperature of the furnace was slowly raised to just above the melting point of the salt mixture. Changes in composition of PbCl_2 -alkali metal chloride mixtures due to volatilization of lead chloride during the melting process were reduced by placing a platinum foil cover over the crucible during the fusion of such mixtures, and as an added precaution the alkali chlorides were placed on top of the lead chloride in the crucible.

Mixtures were analyzed after the completion of a set of measurements. Those mixtures containing silver nitrate were

analyzed for Ag^+ by the Volhard method. The NaCl-KCl mixture was analyzed for total Cl^- by the Volhard method (36).

The PbCl_2 -alkali metal chloride melts were treated in the following way: The weighed samples were dissolved in hot water and then cooled. The lead chloride which precipitated out was filtered off and weighed. The filtrate was then titrated for Pb^{++} with the disodium salt of 1,2-cyclohexanediaminetetraacetic acid (Hach Chemical Company, Ames, Iowa) using the method of Loomis (37). The amount of Pb^{++} was then expressed as lead chloride and added to the initial weight of lead chloride.

Measurement of the surface tension

After fusion and thorough stirring of the melt with a quartz rod, the transite plug was placed in the top of the furnace core and the measuring thermocouple lowered into its position. Proper adjustment of the sensitivity of the controller was made and the system was brought to constant temperature. The capillary, whose tip had been carefully inspected for damage, faced, reamed, and remeasured if necessary, was attached to the apparatus and lowered by means of the winch to within a very short distance from the surface of the melt. Helium gas was passed slowly through the system in order to expel all air from it. The capillary was then

carefully lowered by means of the micrometer head until it touched the surface of the melt. This point was determined in the following way: An electrical circuit consisting of the wire welded to the platinum crucible, milliammeter, power supply, and the capillary with appropriate connecting wires was arranged. When the capillary touched the surface of the melt, completion of the circuit was indicated by deflection of the needle on the milliammeter. Although previous investigators had located the surface either by visual means or by noting the precise moment when there was a sudden rise in the pressure of the system due to contact of the capillary with the surface, the author found that locating it by electrical contact was much easier.

After the surface was located, the capillary was lowered a known distance into the melt by rotating the micrometer head. The accuracy of the vertical displacement of the capillary by the micrometer was checked by comparing readings on the micrometer with the displacement of the tip measured with the cathetometer. The difference in vertical displacement indicated by the micrometer was accurate to within ± 0.005 cm; however, this is the limit of accuracy with which the cathetometer could be read and does not refer to the accuracy with which the micrometer can be set.

For those systems for which density data were not available, measurements were made with the capillary tip at the

surface of the melt. Although temperature fluctuations might be assumed to be at a maximum at the surface, the surface tension measurements on pure salts and mixtures for which density data were available were found to be the same within experimental error with the capillary tip at the surface and with the capillary immersed in the melt. These measurements showed that the surface tension could be accurately measured with the capillary just touching the liquid surface and thus eliminated the need for precise density determinations.

The gas pressure was adjusted by means of the needle valve so that bubbles formed very slowly. Manometer readings were generally made with a bubble rate of one bubble every forty to sixty seconds. Several bubbles were released to promote homogeneity of the melt. The high and low sides of the manometer were followed alternately for four or more bubbles and if reproducible values were obtained, the difference was recorded as the maximum pressure; the temperature was then measured.

The reproducibility of the manometer heights is a decisive criterion for deciding whether or not the true equilibrium pressure in the gas bubble has been measured. Even when the time of bubble formation is varied, the manometer height difference should be exactly reproducible if the system is at equilibrium. By experience it is possible to estimate the

reliability of a particular measurement simply from the peculiar motion of the manometer liquid.

After completion of a successful pressure measurement, the capillary was raised out of the furnace, detached from the apparatus, washed with distilled water and acetone, and reconnected to the apparatus. The cycle of pressure and temperature measurement was repeated at least two more times.

The controller was then adjusted to a higher temperature and the procedure repeated. In this way the surface tension-temperature curves were determined.

The accuracy of the method was checked by making surface tension measurements on benzene. 'Baker Analyzed' Reagent benzene meeting A. C. S. specifications was further purified by distillation through a 30 plate Oldershaw column at a reflux ratio of 10 to 1. The benzene was thermostated at $25.0 \pm 0.1^{\circ}\text{C}$ and its surface tension was determined with the capillary immersed at various known depths in the melt. Very satisfactory agreement with the literature value was obtained; deviations of the experimentally measured surface tensions from the literature value were never greater than 0.5%.

Periodic checks of the accuracy of the method were made during the course of a series of measurements and always after the capillary had undergone some physical or chemical damage which required its being reworked and the bore remeasured.

RESULTS

Surface tension data for the seven pure fused salts and nine binary mixtures investigated are given in Tables 1-10. In no case except that of pure PbCl_2 should the error in these data be greater than 1%. Schroedinger's equation (31) for the relationship between surface tension and maximum bubble pressure was used in all the calculations. For purposes of calculation, this equation is better expressed in the equivalent form:

$$\gamma = \frac{rg}{2} (h d_1 - l d_2) - \frac{1}{3} d_2 r^2 g - \frac{1}{12} \frac{r^3 g d_2^2}{h d_1 - l d_2}$$

where γ is the surface tension in dynes/cm, g is the acceleration due to gravity, h is the manometer height difference in cm of dibutyl phthalate, d_1 is the density of the dibutyl phthalate, l is the depth of immersion of the capillary tip, and d_2 is the density of the melt. Both Jaeger (8,9) and Semenchenko and Shikhobalova (10) asserted erroneously that the second term in the above equation, $1/3 d_2 r^2 g$, was very small compared with experimental error. Their mistake arose from the omission of the acceleration constant, g , in the second and third terms of their equations; the second term contributes 1-2% to the surface tension. The third term in

Table 1. Surface tensions of pure fused salts

| Salt | Temp. °C | Surface tension (dynes/cm) | Salt | Temp. °C | Surface tension (dynes/cm) |
|-------------------|-------------|----------------------------------|-------------------|-------------|----------------------------------|
| NaNO_3^a | 316 | 119.6 | NaNO_3^a | 451 | 110.5 |
| | 317 | 119.6 | | 451 | 111.0 |
| | 319 | 119.0 | | 505 | 107.2 |
| | 320 | 119.3 | | 504 | 107.4 |
| | 338 | 117.3 | KNO_3^a | 358 | 111.9 |
| | 344 | 117.7 | | 358 | 111.8 |
| | 345 | 117.6 | | 398 | 109.6 |
| | 349 | 117.2 | | 398 | 108.7 |
| | 369 | 115.7 | | 419 | 106.9 |
| | 372 | 116.3 | | 420 | 107.0 |
| | 376 | 115.7 | | 454 | 104.2 |
| | 399 | 114.5 | | 454 | 104.3 |
| | 399 | 114.7 | | 473 | 102.9 |
| | 400 | 114.9 | | 473 | 102.9 |
| | 420 | 113.0 | | 494 | 101.5 |
| | 424 | 113.0 | | 496 | 101.3 |
| | 463 | 109.7 | | 546 | 97.0 |
| | 474 | 109.7 | | 546 | 97.6 |
| | 528 | 106.4 | | 594 | 93.8 |
| | 530 | 106.3 | | 595 | 93.8 |
| | 593 | 102.5 | AgNO_3^a | 222 | 147.9 |
| | 596 | 102.2 | | 223 | 149.2 |
| | 351 | 117.3 | | 226 | 148.8 |
| | 351 | 116.7 | | 232 | 149.1 |
| | 352 | 116.6 | | 232 | 148.0 |
| | 376 | 115.4 | | 242 | 147.3 |
| | 375 | 115.7 | | 245 | 146.6 |
| | 400 | 113.8 | | 248 | 147.5 |
| | 400 | 114.3 | | 253 | 147.2 |
| | 401 | 114.4 | | 268 | 146.3 |
| | 428 | 112.5 | | 269 | 146.7 |
| | 428 | 112.6 | | 274 | 145.7 |
| | | | | 278 | 146.5 |
| | | | | 294 | 144.3 |
| | | | | 299 | 143.9 |

^aThe density data used in calculating these surface tensions were those given by Bloom and Rhodes (38).

Table 1. (Continued)

| Salt | Temp. °C | Surface tension (dynes/cm) | Salt | Temp. °C | Surface tension (dynes/cm) |
|--------------------------------|-------------|----------------------------------|--------------------------------|-------------|----------------------------------|
| AgNO ₃ ^a | 318 | 143.1 | KCl ^b | 810 | 97.3 |
| | 322 | 142.3 | | 810 | 98.1 |
| | 344 | 140.7 | | 812 | 97.2 |
| | 349 | 142.5 | | 812 | 98.2 |
| | 352 | 140.2 | | 823 | 96.9 |
| NaCl ^b | 826 | 115.5 | | 840 | 95.3 |
| | 843 | 113.8 | | 844 | 95.7 |
| | 847 | 112.8 | | 846 | 95.5 |
| | 851 | 113.4 | | 858 | 94.2 |
| | 853 | 112.3 | | 859 | 94.3 |
| | 860 | 111.6 | | 901 | 91.0 |
| | 874 | 110.0 | | 902 | 91.0 |
| | 875 | 111.5 | | 903 | 90.8 |
| | 876 | 111.5 | | | |
| | 901 | 109.5 | | 811 | 98.5 |
| | | | | 811 | 98.4 |
| | 902 | 109.1 | | 811 | 98.0 |
| | 905 | 108.8 | | 814 | 98.3 |
| | 935 | 106.8 | | 856 | 94.7 |
| | 937 | 106.8 | | | |
| | | | | 856 | 94.4 |
| | | | | 856 | 94.3 |
| LiCl ^b | 633 | 128.4 | | 869 | 94.0 |
| | 634 | 128.7 | | 874 | 93.3 |
| | 634 | 128.5 | | | |
| | 645 | 128.0 | | | |
| | 646 | 128.0 | PbCl ₂ ^c | 518 | 134.1 |
| | | | | 522 | 135.0 |
| | 662 | 127.6 | | 526 | 135.0 |
| | 666 | 126.7 | | 526 | 135.0 |
| | 667 | 126.7 | | 552 | 131.3 |
| | 681 | 125.5 | | | |
| | 682 | 125.5 | | 552 | 131.0 |
| | | | | 572 | 128.4 |
| | 683 | 125.5 | | | |
| | 706 | 125.0 | | | |
| | 707 | 124.3 | | | |
| | 707 | 124.4 | | | |
| | 710 | 124.1 | | | |

^bDensity data given by Van Artsdalen and Yaffe (39).^cDensity data given by Kortum and Bockris (40).

Table 2. Surface tension in the system $\text{KNO}_3\text{-NaNO}_3^a$

| Mole % NaNO_3 | Temp. $^{\circ}\text{C}$ | Surface tension (dynes/cm) |
|---------------------------|-----------------------------|----------------------------------|
| 44.2 | 351 | 114.0 |
| | 351 | 113.8 |
| | 351 | 114.0 |
| | 393 | 111.3 |
| | 397 | 111.0 |
| | 398 | 110.6 |
| | 444 | 107.0 |
| | 444 | 107.0 |
| 64.1 | 349 | 114.9 |
| | 349 | 115.0 |
| | 398 | 111.7 |
| | 401 | 111.8 |
| | 440 | 109.2 |
| | 449 | 108.3 |

^aDensity data given by Goodwin and Mailey (41).

Table 3. Surface tension in the system $\text{AgNO}_3\text{-NaNO}_3^a$

| Mole % NaNO_3 | Temp. $^{\circ}\text{C}$ | Surface tension (dynes/cm) | Mole % NaNO_3 | Temp. $^{\circ}\text{C}$ | Surface tension (dynes/cm) |
|---------------------------|-----------------------------|----------------------------------|---------------------------|-----------------------------|----------------------------------|
| 9.52 | 302 | 137.0 | 57.13 | 302 | 126.0 |
| | 304 | 137.0 | | 305 | 125.6 |
| | 309 | 137.3 | | 326 | 124.7 |
| | 327 | 136.1 | | 326 | 124.4 |
| | | | | 328 | 124.3 |
| | 327 | 135.9 | 80 | | |
| | 328 | 136.3 | | 316 | 122.2 |
| | 352 | 134.6 | | 317 | 121.8 |
| | 354 | 134.5 | | 319 | 121.4 |
| | | | | 319 | 121.7 |
| 18.16 | 248 | 140.5 | | | |
| | 250 | 138.9 | | 344 | 120.4 |
| | 254 | 138.9 | | 344 | 120.4 |
| | 296 | 135.0 | | 345 | 120.5 |
| | | | | 368 | 118.5 |
| | 300 | 135.9 | | 368 | 118.4 |
| | 300 | 135.9 | 86.33 | | |
| | 303 | 135.9 | | 322 | 120.7 |
| | 303 | 135.9 | | 322 | 120.3 |
| | | | | 352 | 118.3 |
| | 325 | 134.1 | | 352 | 118.9 |
| | 328 | 134.3 | | | |
| | 329 | 134.1 | | 376 | 117.2 |
| | 356 | 132.3 | | 376 | 117.3 |
| | | | | 390 | 115.8 |
| | | | | 398 | 115.6 |
| 40 | 269 | 131.7 | | | |
| | 271 | 132.8 | | | |
| | 272 | 133.4 | | | |
| | 302 | 129.4 | | | |
| | | | | | |
| | 302 | 129.6 | | | |
| | 328 | 128.6 | | | |
| | 329 | 128.5 | | | |

^aDensity data given by Byrne, Fleming, and Wetmore (42).

Table 4. Surface tension in the system $\text{AgNO}_3\text{-KNO}_3^a$

| Mole % KNO_3 | Temp. $^{\circ}\text{C}$ | Surface tension (dynes/cm) | Mole % KNO_3 | Temp. $^{\circ}\text{C}$ | Surface tension (dynes/cm) |
|--------------------------|-----------------------------|----------------------------------|--------------------------|-----------------------------|----------------------------------|
| 8.12 | 252 | 139.7 | 71.60 | 276 | 119.3 |
| | 252 | 138.9 | | 276 | 119.4 |
| | 256 | 138.5 | | 298 | 117.4 |
| | 304 | 135.3 | | 302 | 117.4 |
| | 306 | 135.5 | | 302 | 117.8 |
| | 324 | 134.8 | | 322 | 115.9 |
| | 325 | 133.8 | | 323 | 115.6 |
| | 326 | 134.3 | | 325 | 116.3 |
| | 356 | 132.8 | | 355 | 114.0 |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| 29.58 | 254 | 132.0 | 87.05 | 324 | 115.1 |
| | 254 | 132.3 | | 324 | 115.8 |
| | 300 | 125.4 | | 325 | 114.8 |
| | 302 | 125.0 | | 326 | 114.6 |
| | 328 | 124.0 | | 351 | 112.6 |
| 52.83 | | | | 352 | 113.5 |
| | 254 | 123.9 | | 352 | 112.3 |
| | 256 | 123.9 | | 353 | 112.3 |
| | 276 | 122.7 | | | |
| | 276 | 122.5 | | | |
| | 296 | 120.7 | | | |
| | 298 | 120.7 | | | |
| | 324 | 118.7 | | | |
| | 324 | 118.7 | | | |
| | 354 | 116.9 | | | |
| | | | | | |

^aDensity data given by Bloom and Rhodes (38).

Table 5. Surface tension in the system NaCl-KCl^a

| Mole % KCl | Temp. °C | Surface tension (dynes/cm) | Mole % KCl | Temp. °C | Surface tension (dynes/cm) |
|---------------|-------------|----------------------------------|---------------|-------------|----------------------------------|
| 20 | 742 | 115.4 | 60 | 697 | 111.6 |
| | 748 | 114.8 | | 698 | 111.1 |
| | 748 | 116.0 | | 729 | 109.2 |
| | 770 | 113.4 | | 729 | 109.2 |
| | 770 | 113.3 | | 774 | 105.4 |
| | 799 | 111.2 | | 776 | 105.6 |
| | 800 | 111.3 | | 797 | 103.8 |
| | 825 | 109.5 | | 798 | 103.9 |
| | 829 | 109.8 | | 826 | 101.2 |
| | | | | 826 | 101.1 |
| 40 | 697 | 114.0 | 60 | 700 | 110.6 |
| | 700 | 114.0 | | 702 | 110.2 |
| | 700 | 113.7 | | 702 | 110.7 |
| | 723 | 112.2 | | 726 | 108.7 |
| | 724 | 111.7 | | 727 | 108.5 |
| | 727 | 112.3 | | 752 | 107.3 |
| | 749 | 110.5 | | 753 | 106.9 |
| | 751 | 110.8 | | 772 | 104.9 |
| | | | | 774 | 104.6 |
| 40 | 748 | 110.7 | 80 | 728 | 106.2 |
| | 749 | 110.8 | | 730 | 106.1 |
| | 752 | 111.0 | | 731 | 105.8 |
| | 770 | 109.2 | | 752 | 104.5 |
| | 772 | 109.0 | | 755 | 104.7 |
| | 822 | 105.3 | | 756 | 104.6 |
| | 824 | 104.6 | | 784 | 103.8 |
| | 824 | 104.6 | | 786 | 102.0 |
| | 825 | 104.9 | | | |

^aDensity data given by Van Artsdalen and Yaffe (39).

Table 6. Surface tension in the system $\text{PbCl}_2\text{-LiCl}$

| Mole % LiCl | Temp. °C | Surface tension (dynes/cm) | Mole % LiCl | Temp. °C | Surface tension (dynes/cm) |
|----------------|-------------|----------------------------------|----------------|-------------|----------------------------------|
| 30.10 | 501 | 133.0 | 50.37 | 500 | 133.9 |
| | 501 | 133.0 | | 500 | 121.7 |
| | 525 | 131.8 | | 500 | 131.9 |
| | 525 | 131.8 | | 526 | 130.7 |
| | 551 | 129.5 | | 526 | 131.0 |
| | 551 | 129.0 | | 550 | 129.0 |
| | 574 | 127.3 | | 550 | 128.7 |
| | 574 | 127.4 | | 576 | 126.2 |
| | 600 | 124.1 | | | |
| 35.75 | 499 | 134.5 | 68.74 | 534 | 129.3 |
| | 501 | 134.5 | | 534 | 129.3 |
| | 525 | 131.8 | | 549 | 128.7 |
| | 552 | 128.8 | | 549 | 127.1 |
| | 575 | 125.5 | | 551 | 127.4 |
| | 576 | 125.5 | 73.63 | 574 | 125.1 |
| 49.39 | 498 | 134.1 | | 574 | 125.3 |
| | 498 | 133.9 | | 575 | 127.2 |
| | 523 | 131.1 | | 599 | 123.6 |
| | 524 | 130.8 | | 600 | 123.6 |
| | 525 | 131.0 | | | |
| | 549 | 128.6 | | | |
| | 550 | 128.7 | | | |
| | 573 | 126.5 | | | |
| | 575 | 126.3 | | | |

Table 7. Surface tension in the system $\text{PbCl}_2\text{-NaCl}$

| Mole % NaCl | Temp. °C | Surface tension (dynes/cm) |
|----------------|-------------|----------------------------------|
| 19.65 | 495 | 133.6 |
| | 500 | 133.1 |
| | 524 | 130.0 |
| | 525 | 129.6 |
| | 551 | 127.0 |
| | 552 | 126.7 |
| | 576 | 124.6 |
| | 577 | 123.9 |
| 38.83 | 495 | 130.9 |
| | 499 | 131.0 |
| | 527 | 127.5 |
| | 531 | 127.2 |
| | 552 | 124.5 |
| | 553 | 124.5 |
| | 578 | 122.1 |
| 45.9 | 567 | 123.1 |
| | 572 | 122.6 |
| | 590 | 120.7 |
| 51.54 | 576 | 121.7 |
| | 580 | 121.7 |

Table 8. Surface tension in the system $\text{PbCl}_2\text{-KCl}^a$

| Mole % KCl | Temp. °C | Surface tension (dynes/cm) |
|---------------|-------------|-------------------------------|
| 24.32 | 495 | 121.4 |
| | 500 | 120.9 |
| 35.88 | 498 | 117.7 |
| | 500 | 117.7 |
| | 525 | 115.1 |
| | 525 | 115.0 |
| | 550 | 112.6 |
| | 574 | 110.2 |
| | 575 | 110.3 |
| 50.87 | 495 | 115.8 |
| | 498 | 115.0 |
| | 525 | 112.5 |
| | 526 | 113.0 |
| | 549 | 110.3 |
| | 550 | 109.8 |
| 51.15 | 490 | 116.0 |
| | 493 | 115.4 |
| | 494 | 115.6 |
| | 495 | 116.0 |
| | 552 | 109.9 |
| | 553 | 109.9 |
| 63.14 | 552 | 110.6 |
| | 553 | 110.6 |
| | 574 | 107.9 |
| | 601 | 106.5 |
| | 601 | 106.3 |
| 68.23 | 592 | 106.2 |
| | 594 | 106.4 |
| | 625 | 103.9 |
| | 625 | 103.9 |
| | 626 | 103.9 |

^aDensity data given by Kortum and Bockris (40).

Table 9. Surface tension in the system $\text{PbCl}_2\text{-RbCl}$

| Mole % RbCl | Temp. °C | Surface tension (dynes/cm) | Mole % RbCl | Temp. °C | Surface tension (dynes/cm) |
|----------------|-------------|----------------------------------|----------------|-------------|----------------------------------|
| 3.96 | 512 | 131.6 | 50.92 | 526 | 107.2 |
| | 512 | 131.4 | | 526 | 107.2 |
| | 528 | 130.3 | | 551 | 105.3 |
| | 528 | 129.6 | | 553 | 105.2 |
| | 528 | 129.6 | | 576 | 102.7 |
| | | | | 576 | 102.7 |
| | 554 | 126.9 | | | |
| | 555 | 126.9 | | | |
| | 576 | 123.8 | | | |
| | 577 | 123.9 | | | |
| 19.80 | | | 55.0 | 474 | 111.7 |
| | | | | 475 | 111.5 |
| | | | | 500 | 109.4 |
| | | | | 500 | 108.9 |
| | | | | 500 | 108.9 |
| | 476 | 123.8 | | | |
| | 478 | 123.5 | | | |
| | 499 | 120.8 | | 524 | 106.7 |
| | 499 | 121.0 | | 524 | 107.1 |
| | 526 | 118.4 | | 576 | 105.6 |
| 31.90 | | | | 577 | 102.3 |
| | 527 | 118.2 | 57.77 | | |
| | 545 | 116.7 | | 472 | 112.4 |
| | 548 | 116.4 | | 474 | 111.8 |
| | 575 | 113.2 | | 476 | 111.9 |
| | | | | 500 | 109.5 |
| | | | | 500 | 109.5 |
| | 473 | 116.7 | | | |
| | 475 | 116.0 | | 524 | 106.8 |
| | 475 | 116.0 | | 524 | 106.7 |
| | 499 | 113.6 | | 550 | 104.4 |
| 50.92 | 499 | 113.2 | 72.50 | | |
| | | | | 566 | 104.8 |
| | 524 | 111.0 | | 566 | 103.5 |
| | 525 | 111.1 | | 567 | 105.2 |
| | 550 | 108.2 | | 567 | 104.9 |
| | 574 | 106.7 | | 579 | 103.5 |
| | | | | | |
| | 472 | 113.0 | | | |
| | 473 | 112.2 | | 587 | 103.0 |
| | 474 | 111.4 | | 588 | 102.6 |
| 50.92 | 500 | 109.9 | | | |
| | 500 | 109.8 | | | |

Table 10. Surface tension in the system $\text{PbCl}_2\text{-CsCl}$

| Mole % CsCl | Temp. °C | Surface tension (dynes/cm) | Mole % CsCl | Temp. °C | Surface tension (dynes/cm) |
|----------------|-------------|----------------------------------|----------------|-------------|----------------------------------|
| 18.10 | 461 | 119.5 | 49.5 | 625 | 91.2 |
| | 470 | 119.6 | | 625 | 91.4 |
| | 497 | 116.5 | | 627 | 90.9 |
| | 498 | 116.5 | | | |
| | 523 | 113.9 | | | |
| | | | 59.89 | 601 | 92.8 |
| | 524 | 113.9 | | 601 | 92.4 |
| | 549 | 110.7 | | 620 | 91.0 |
| | 549 | 111.5 | | 628 | 90.1 |
| | 550 | 111.2 | | 629 | 89.9 |
| | 577 | 108.6 | | | |
| | 577 | 108.6 | | | |
| | | | 74.11 | 498 | 102.9 |
| | | | | 524 | 99.3 |
| | | | | 524 | 100.7 |
| 18.23 | 496 | 116.3 | | 525 | 100.4 |
| | 498 | 116.4 | | 551 | 98.6 |
| | 525 | 113.4 | | | |
| | 527 | 113.1 | | | |
| | 552 | 110.6 | | 552 | 98.5 |
| | | | | 579 | 96.0 |
| | 554 | 110.5 | | 580 | 95.9 |
| | 593 | 106.9 | | 602 | 93.9 |
| | | | | 604 | 93.9 |
| | | | | 630 | 91.4 |
| 36.97 | 584 | 98.0 | | | |
| | 585 | 99.5 | | | |
| | 596 | 97.1 | | | |
| | 597 | 96.9 | | | |
| | 618 | 94.5 | | | |

the Schrodinger equation definitely is negligible, of the order of 10^{-4} dynes/cm.

The expansion of the capillary bore with increasing temperature was taken into account in all the calculations. Since no information was available on the thermal expansion of 90% platinum-10% rhodium alloy, the coefficients of expansion for the 80% platinum-20% rhodium alloy were used instead. The expression (43) for the linear expansion of the 80% alloy is

$$l_t = l_0(1 + 8.79 \times 10^{-6} t + 1.61 \times 10^{-9} t^2)$$

where l_0 is the length at 0°C and l_t is the length at the temperature t .

Density data needed in the calculations were taken from the most reliable literature sources; reference to the source of these data for each particular pure salt and fused salt mixture is indicated in the tables of surface tension data (Tables 1-10). No density data were available for the systems PbCl_2 - LiCl , PbCl_2 - NaCl , PbCl_2 - RbCl , and PbCl_2 - CsCl . The surface tensions of these systems were measured with the capillary tip at the surface of the melt as pointed out in the "Procedure". As a result there was no need to correct for the hydrostatic pressure, ld_2g , due to depth of immersion of the capillary. This eliminated the need for precise density data. In order to calculate the second term of the equation, density values at

various compositions were estimated by interpolations from the straight lines connecting the densities of the pure salts at the temperatures of interest. The error introduced in the surface tension by this approximation should be negligible since the density-composition isotherms for fused salt mixtures are in general essentially linear.

The value of g at Ames, Iowa was calculated from Helmert's equation (44) and found to be 980.26 cm/sec^2 .

No correction was made for capillary rise of the salt in the containing crucible. Sugden (32) showed that the central portion of the meniscus would have a negligible radius of curvature only if containers several centimeters in diameter were used. Since the crucible used in this work had a diameter of 5 cm, the error due to capillary rise in the containing vessel is negligible.

The surface tension data for the various mixtures were treated in the following way. Surface tension was plotted against temperature at each composition. The best smooth curve was drawn through these points; usually the best fit was a straight line. Surface tension values at various compositions were obtained from these graphs and from these values surface tension-composition isotherms were constructed.

DISCUSSION

Pure Fused Salts

The surface tension-temperature curves for the pure fused salts investigated are shown in Figures 4 and 5. Although no surface tension data for zinc chloride are listed in Table 1, a sufficient number of measurements were made to establish that its surface tension is very low, approximately 56 dynes/cm at 450° C. The curves in Figures 4 and 5 show an essentially linear variation of surface tension with temperature.

One would expect the surface energy, $\gamma - T(\partial\gamma/\partial T)$, of ionic melts to be determined chiefly by the electrostatic forces between the ions in the surface; thus molten NaCl would be expected to have a higher surface energy than molten KCl. In the case of the salts investigated the trends in total surface energy parallel the trends in surface tension shown in Figures 4 and 5. The correlation of surface energy with electrostatic forces works quite well for the chlorides and alkali metal nitrates. However, it is complicated by the fact that the surface energy of AgNO_3 is higher than that of NaNO_3 . From this it is apparent that the forces between the ions in a silver nitrate melt are stronger than those in a sodium nitrate melt. In the absence of concrete experimental data this can possibly be attributed to (a) smaller interionic

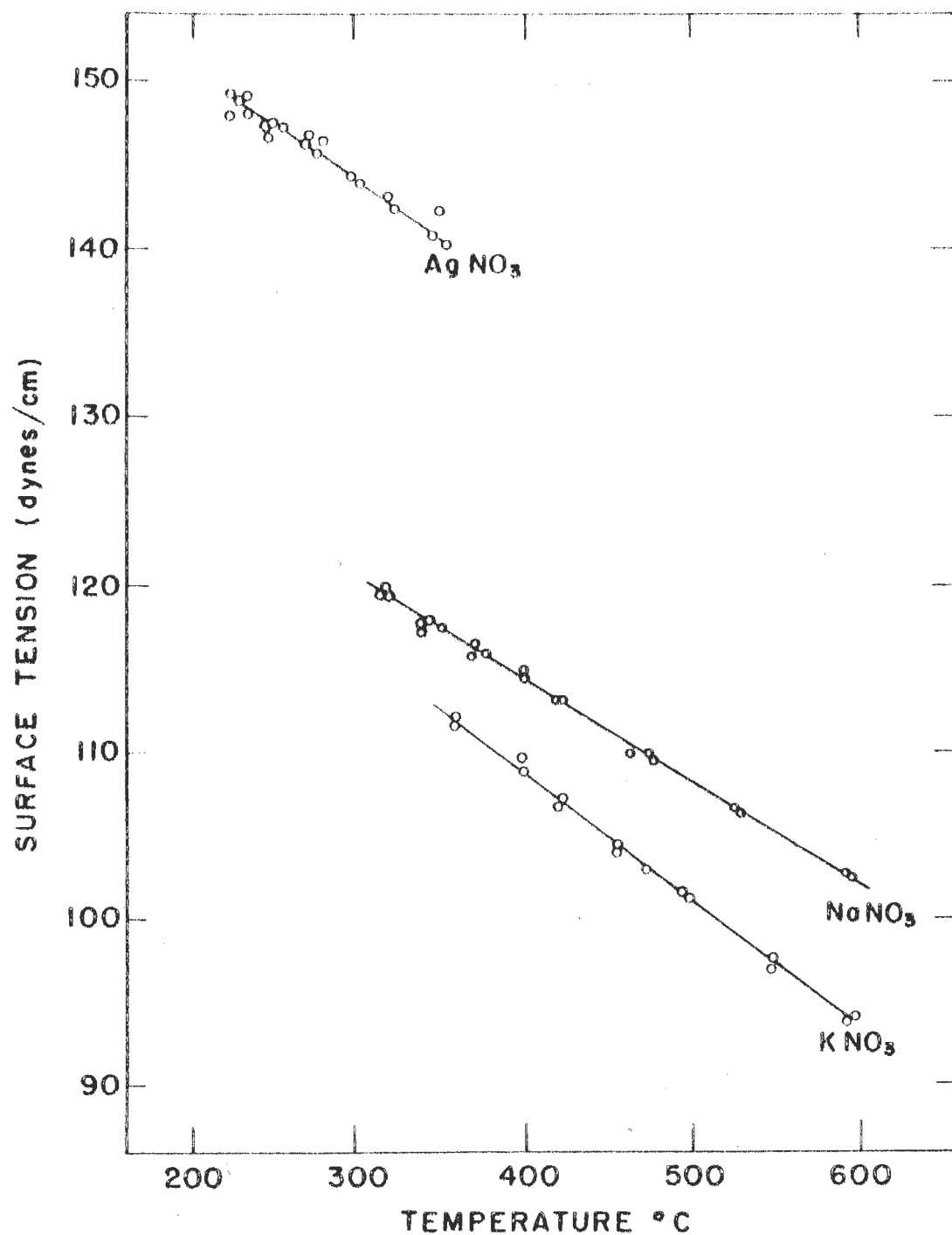


Figure 4. Surface tensions of pure fused nitrates

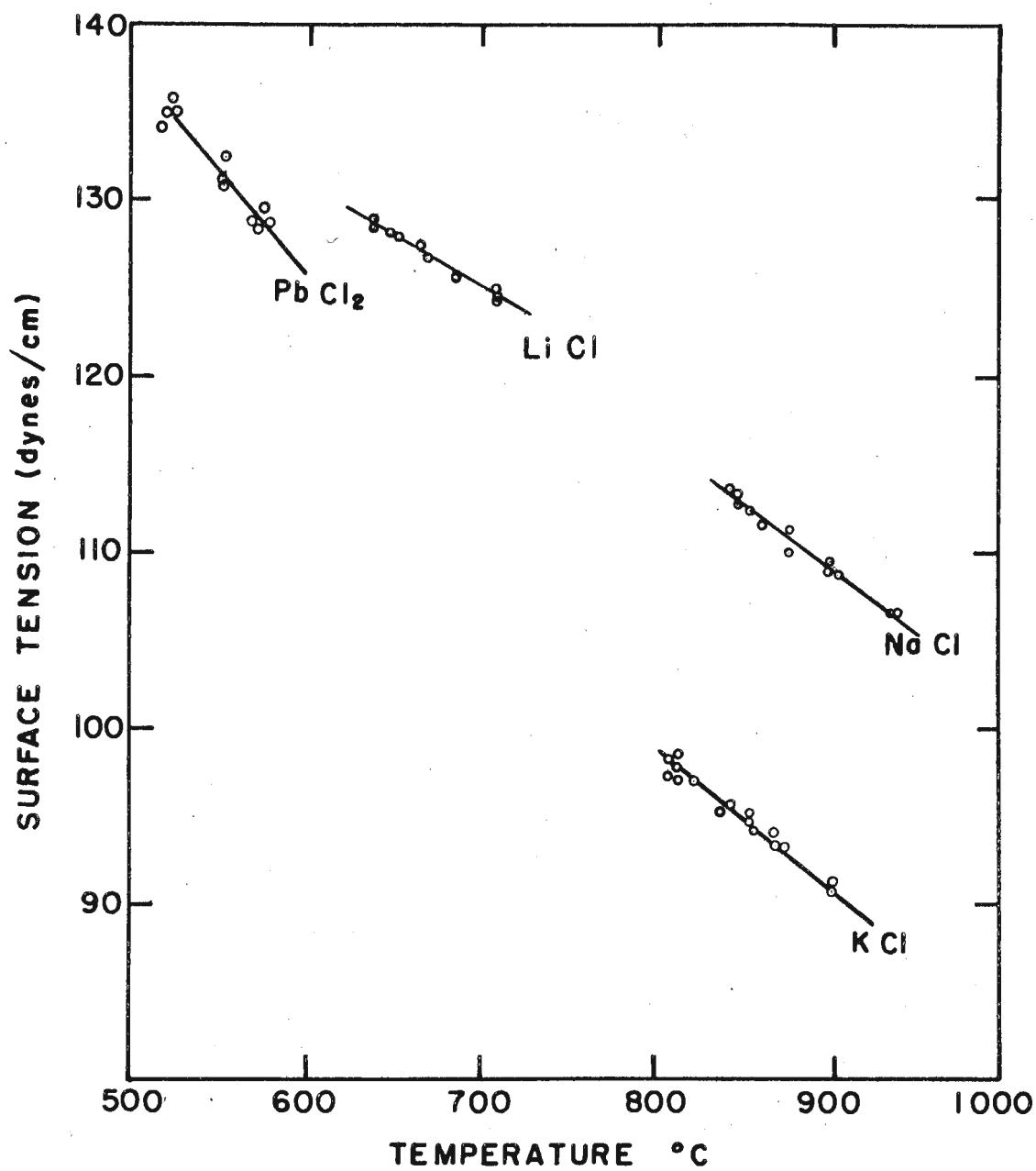


Figure 5. Surface tensions of pure fused chlorides

separation in a silver nitrate melt compared to a sodium nitrate despite the fact that the radii of the metal ions are approximately the same in the solid state, (b) increased covalent character in the interactions in a silver nitrate melt compared to a sodium nitrate melt due to the fact that the eighteen electron shell of a transition type ion like silver ion is more easily deformed (polarized) than is the inert gas type shell.

The high surface energy of molten PbCl_2 argues strongly against the presence of PbCl_2 molecules in this melt.

Molten zinc chloride and cadmium chloride have abnormally low surface energies compared with other melts containing ions of similar charge and size. A Raman investigation by Bues (45) of molten cadmium chloride and molten zinc chloride showed great resemblance between the spectra of these compounds in the liquid and in the solid state, thereby indicating similar structures in the solid and liquid. It is very interesting to note that these crystalline salts are isomorphous and possess the layer-lattice cadmium chloride type structure. The cadmium atoms are at the centers of octahedra which are joined together in sheets held together mainly by van der Waals forces. The persistence of such a structure in the liquid would explain the low conductivity of these melts. The low surface energies of these liquids may be attributed to the

fact that it is energetically an easy process to separate these sheets and form new surface.

The surface tension data for molten potassium nitrate agree with the data reported by Jaeger (9) within 0.1%. The data for NaNO_3 are 1.5% lower than those reported by Jaeger (9). There are no data in the literature on AgNO_3 . Surface tension data for KCl reported in Table 1 are some 2.5% higher than those reported by Jaeger (9), but agree within 0.5% with those given by Semenchenko and Shikhobalova (11). The data for NaCl are 1.8% higher than those reported by Jaeger, but agree within 0.5% with those reported by Semenchenko and Shikhobalova (11). Jaeger's data (9) for LiCl are 5.3% higher than those listed in Table 1. For PbCl_2 the data differ from Jaeger's (9) by approximately 2%; his surface tension-temperature curve was by no means linear. Other literature values for PbCl_2 (13) vary as much as 10%, the greater variance being due no doubt to the high volatility of the melt.

Binary Mixtures

Surface tension-composition isotherms for the binary fused salt mixtures studied are shown in Figures 6-14.

Statistical treatments of the dependence of the surface tension of a binary mixture on its composition have been carried out by Belton and Evans (46) and by Guggenheim (47).

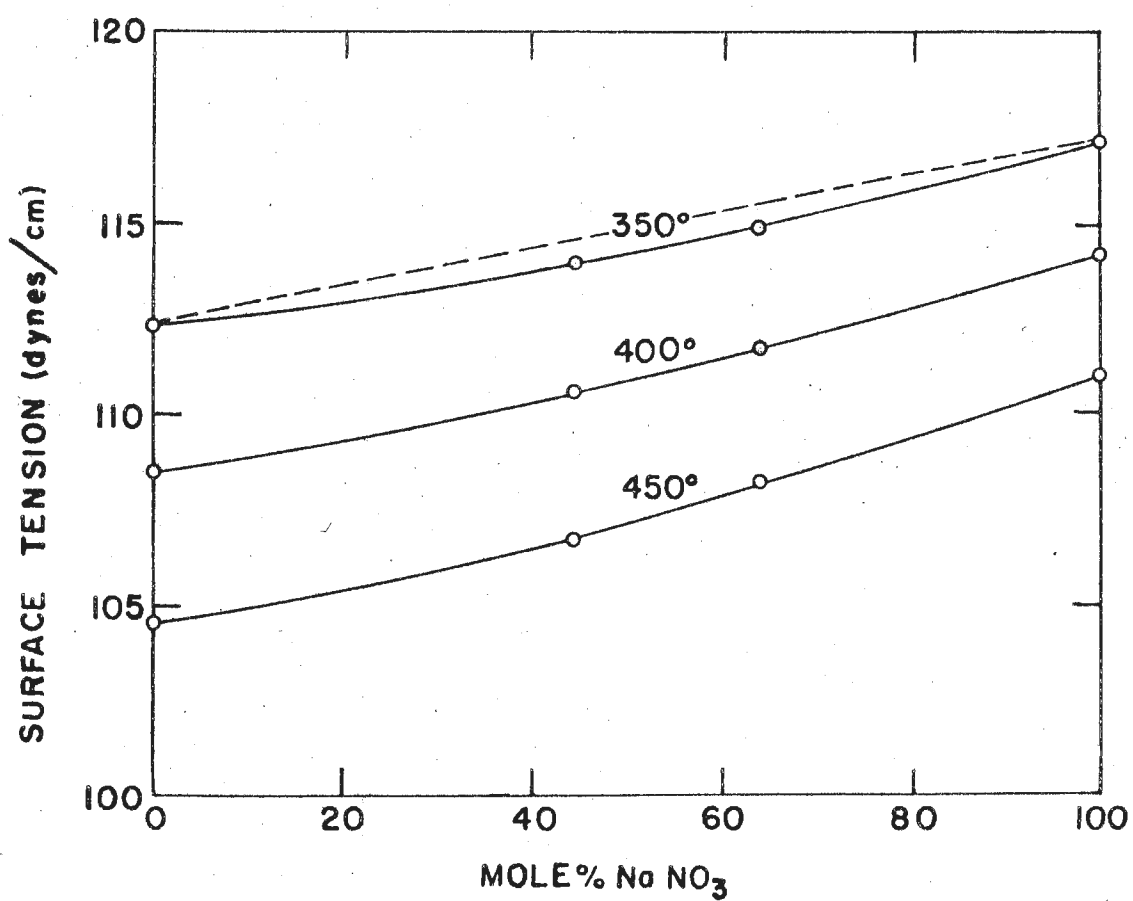


Figure 6. Surface tension isotherms in the system $\text{NaNO}_3\text{-KNO}_3$
(Dashed curve is the ideal 350° surface tension isotherm)

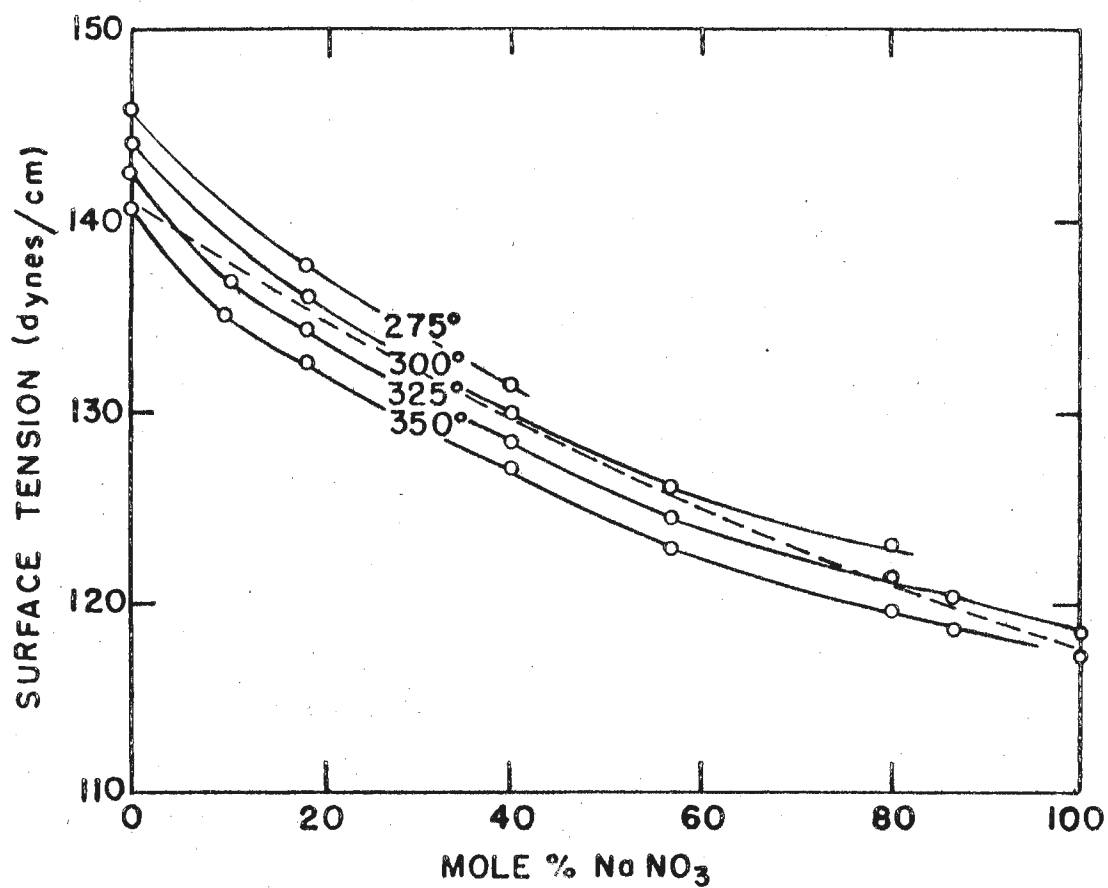


Figure 7. Surface tension isotherms in the system $\text{AgNO}_3\text{-NaNO}_3$
(Dashed curve is the ideal 350° surface tension isotherm)

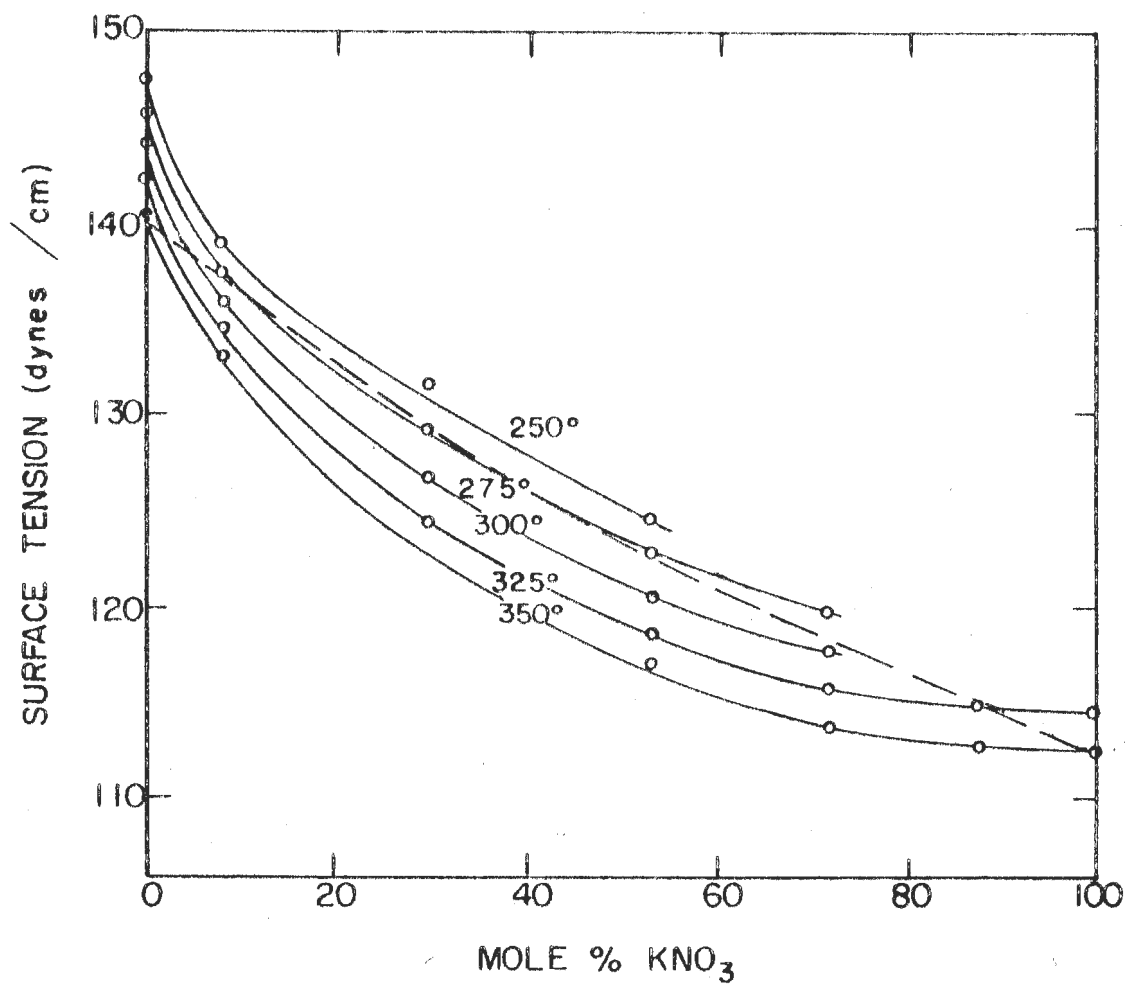


Figure 8. Surface tension isotherms in the system $\text{AgNO}_3\text{-KNO}_3$

(Dashed curve is the ideal 350° surface tension isotherm)

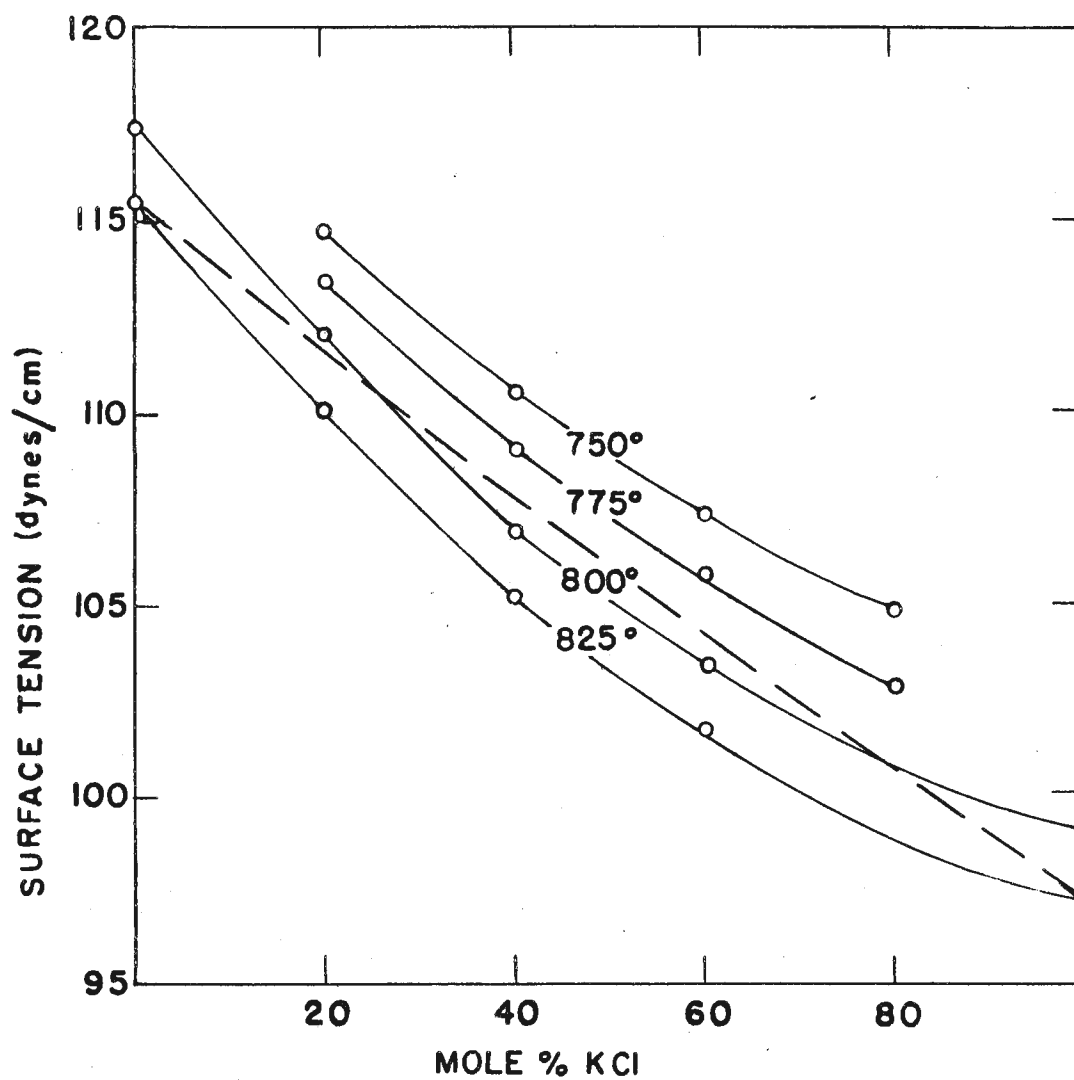


Figure 9. Surface tension isotherms in the system NaCl-KCl

(Dashed curve is the ideal 825° surface tension isotherm)

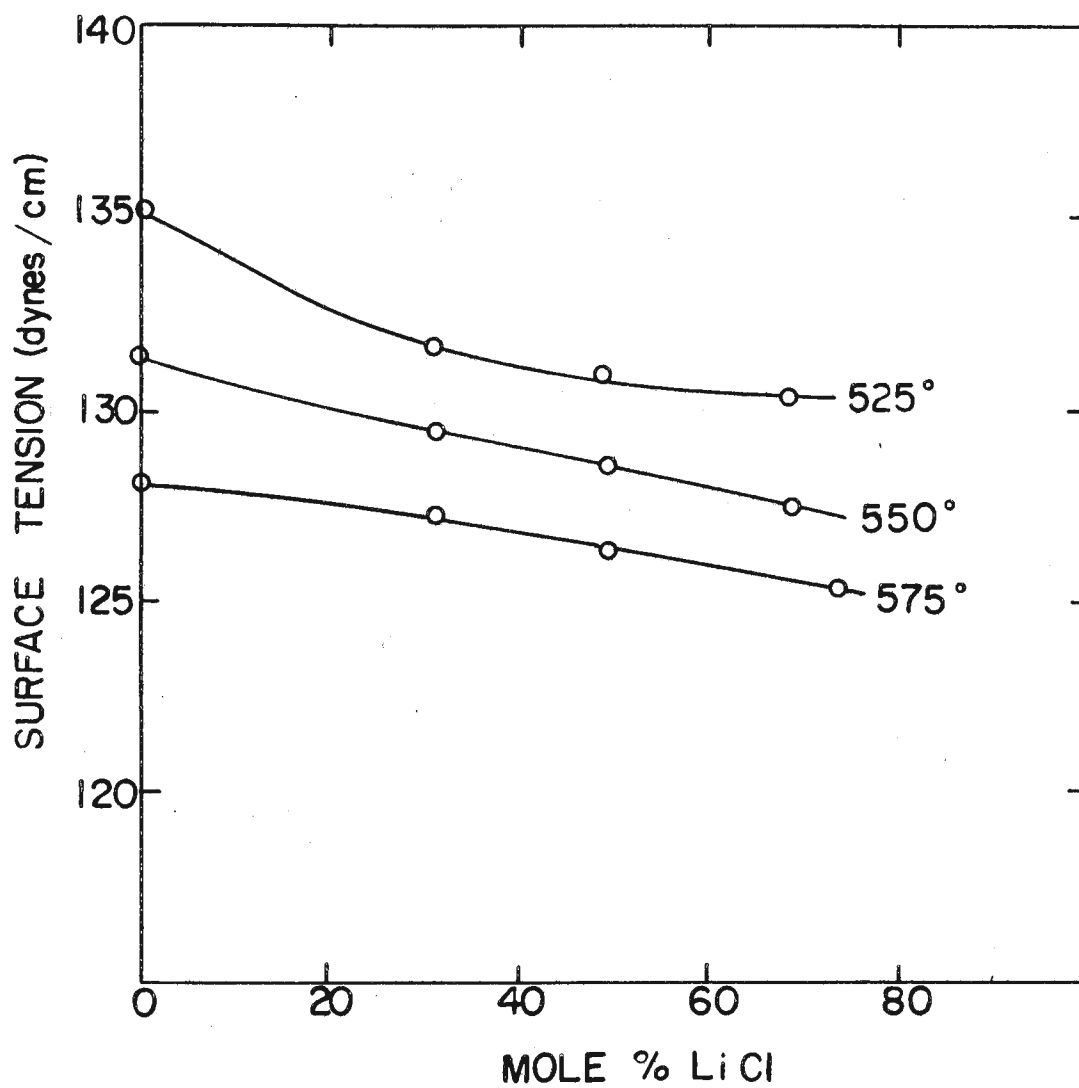


Figure 10. Surface tension isotherms in the system PbCl_2 - LiCl

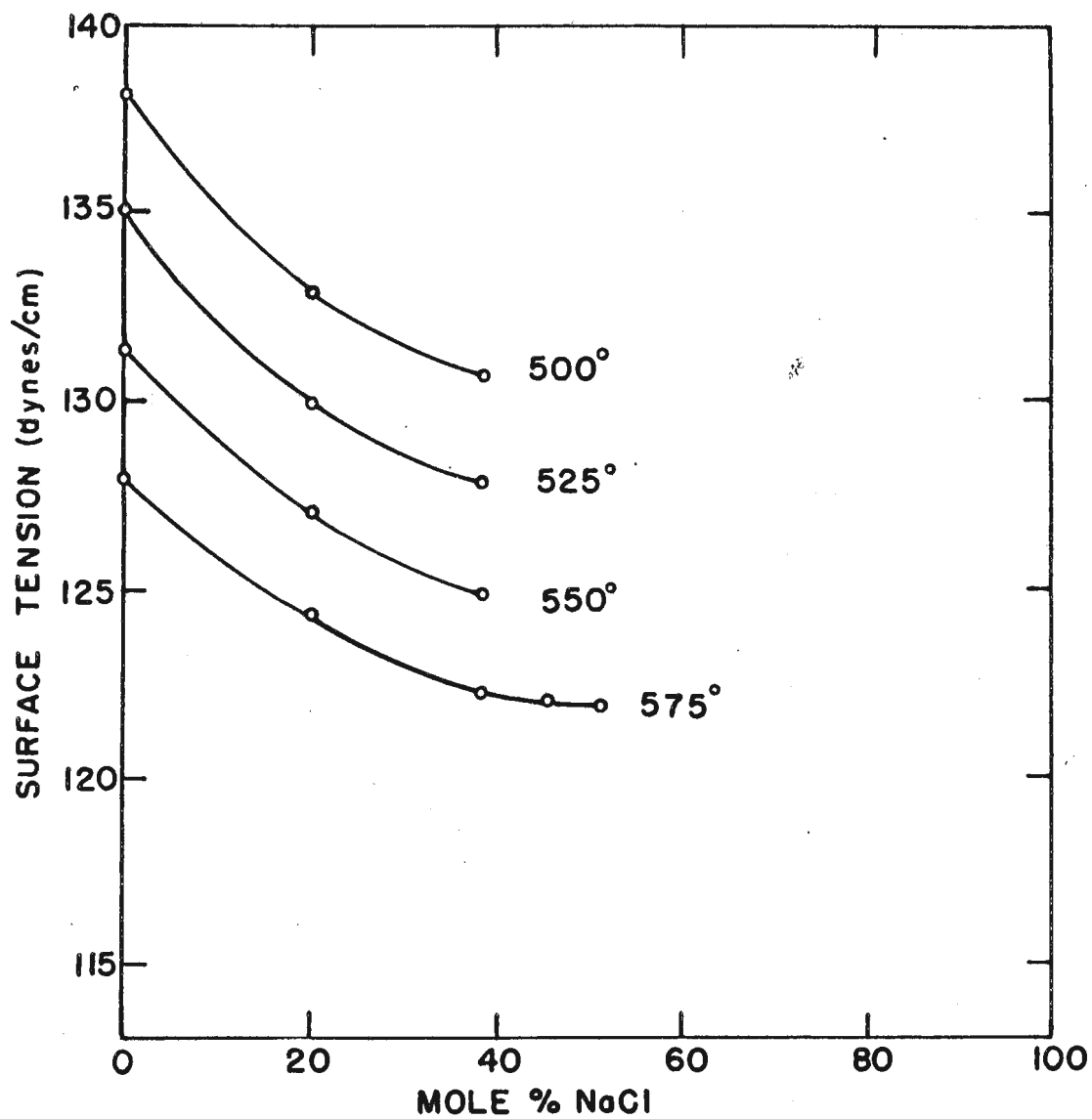


Figure 11. Surface tension isotherms in the system $\text{PbCl}_2\text{-NaCl}$

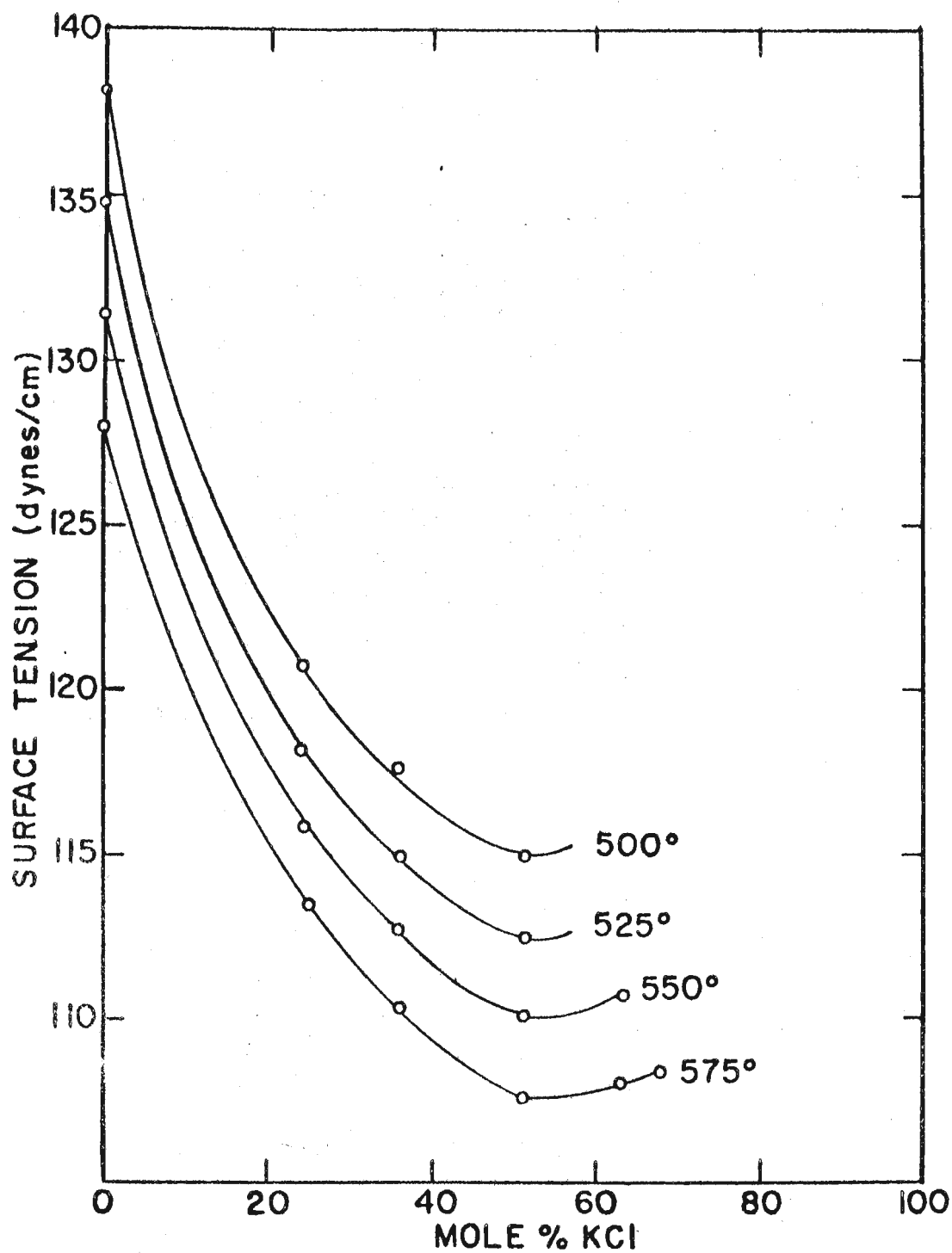


Figure 12. Surface tension isotherms in the system PbCl_2 -KCl

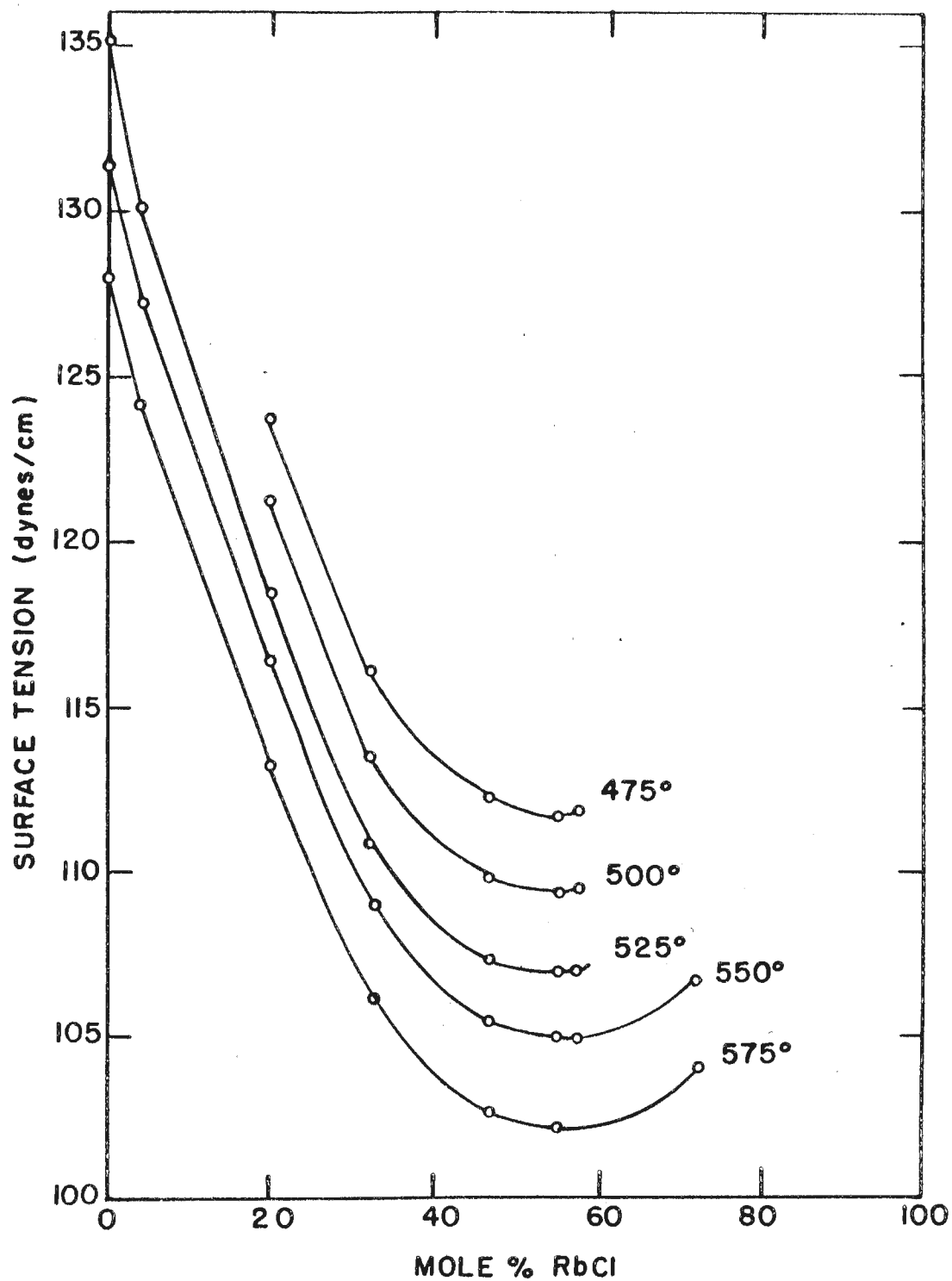


Figure 13. Surface tension isotherms in the system $\text{PbCl}_2\text{-RbCl}$

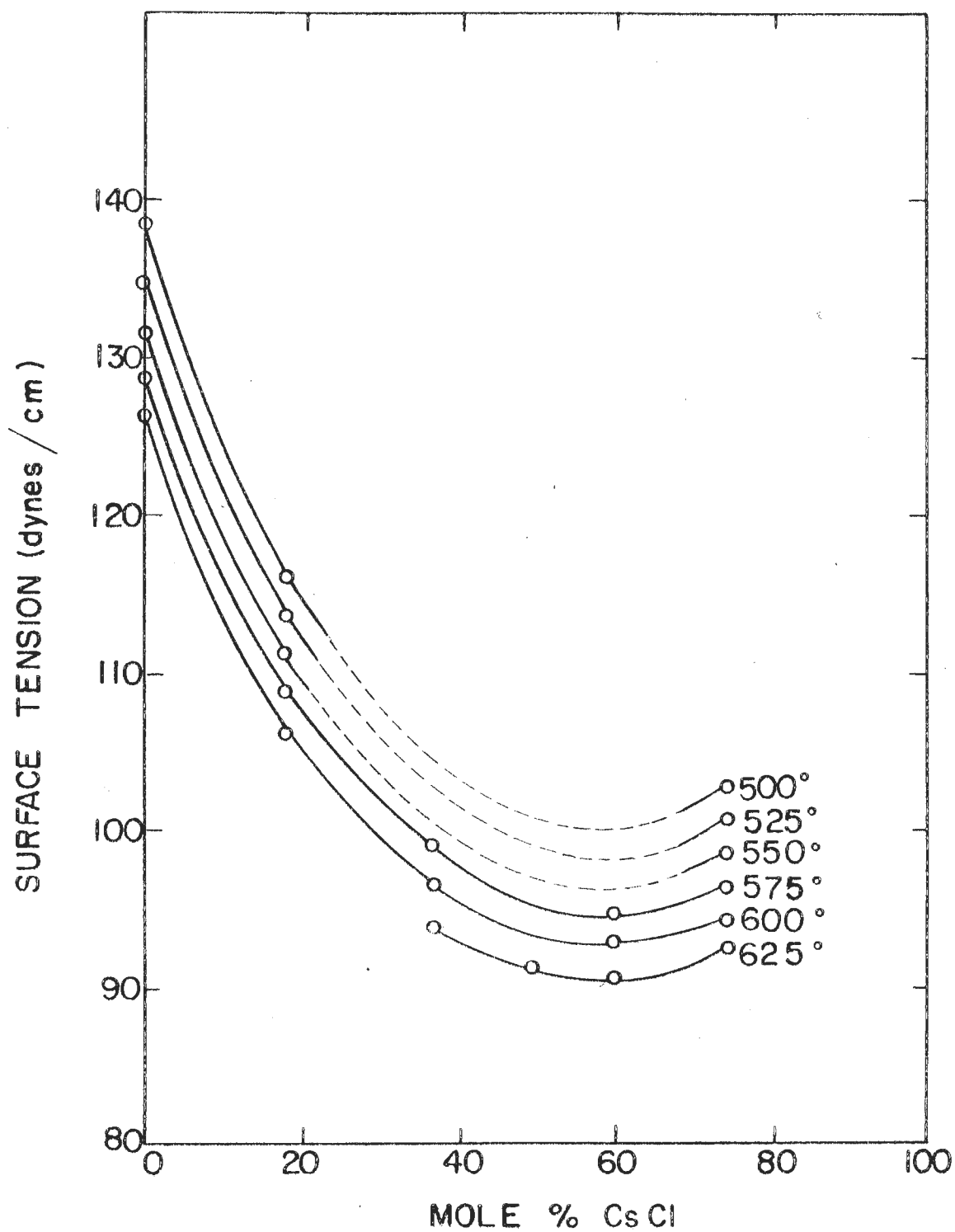


Figure 14. Surface tension isotherms in the system $\text{PbCl}_2\text{-CsCl}$

For the case of a perfect (ideal) solution Guggenheim (47) gives the equation

$$\exp - \frac{\gamma a}{kT} = x_A \exp - \frac{\gamma_A a}{kT} \quad x_B \exp - \frac{\gamma_B a}{kT}$$

where γ is the surface tension of the mixture, γ_A and γ_B are the surface tensions of the pure components, x_A and x_B are the mole fractions of A and B in the bulk, a is the average area per molecule in the surface layer, k is the Boltzmann constant, and T is the absolute temperature.

For the special case of an equimolar mixture where $x_A = x_B = \frac{1}{2}$, Guggenheim (47) reduced the above equation to

$$\gamma = \frac{1}{2}(\gamma_A + \gamma_B) - \frac{(\gamma_B - \gamma_A)^2 a}{8kT}.$$

This latter equation was utilized by Boardman, Palmer, and Heymann (16) to calculate deviations from ideality of the surface tensions of equimolar mixtures of various molten salts. They calculated the mean area of the molecules from the molar volume of the mixture according to the formula

$$a = \frac{1}{2}(M_A/Nd_A)^{2/3} + \frac{1}{2}(M_B/Nd_B)^{2/3},$$

where M and d are the molecular weight and density respectively of the particular components and N is Avagadro's number.

In order to obtain a more convenient surface tension equation applicable at any molar composition, the first equation given by Guggenheim (47) was transformed by mathematical expansions to give the simple equation

$$\gamma = (x_A \gamma_A + x_B \gamma_B) - \frac{x_A x_B (\gamma_B - \gamma_A)^2 a}{2kT}.$$

For the special case of an equimolar composition, this equation becomes identical to Guggenheim's second equation. This equation was found to be sufficiently accurate to calculate the theoretical ideal surface tension isotherms for the systems KCl-NaCl and NaNO₃-KNO₃. For the AgNO₃-alkali metal nitrate melts where $(\gamma_B - \gamma_A)$ is not small compared to the first term in the equation, higher order terms must be considered. The mean area of the molecules was calculated from the equation

$$a = x_A (M_A / N_A)^{2/3} + x_B (M_B / N_B)^{2/3}.$$

The ideal surface tension isotherms are shown as dashed curves in Figures 6-9. Ideal curves were not calculated for the PbCl₂-alkali metal chloride systems since such calculation necessitates extrapolation of the surface tensions of the pure alkali metal chlorides to temperatures far below the melting points of the salts.

Differences between the observed and calculated ideal surface tension isotherms may arise from several causes. Deviations from ideality may arise because: (a) the molecular packing of the two components is different (the assumption that both species have the same number of nearest neighbors and pack in the same way as in the pure liquids is incorporated into the statistical formulation of the theory), (b) the areas of the molecules may not be the same (the theory strictly holds only for equal molecular areas); in addition, the average molecular area of the surface may not be the same as that calculated from the density of the bulk, (c) the heat of mixing of the two components may not be zero, (d) the surface discontinuity between the phases may not be restricted to a single molecular area as is assumed in the theoretical treatment.

The system $\text{NaNO}_3\text{-KNO}_3$ was investigated first in order to check the reliability of the maximum bubble pressure method in work on mixtures. The shape of the surface tension isotherms is exactly the same as that obtained by Boardman, Palmer, and Heymann (16); the absolute values are different. This is not surprising since Boardman, Palmer, and Heymann (16) measured all their surface tensions relative to tap water. Since the surface tensions of the two pure salts are so similar, the calculated ideal surface tension curve is essentially a straight line. The ideality of the experimental surface tension isotherms (Figure 6) is in accord with other physical measurements

which have been made on this system. Equivalent conductivities (41), molar volumes (41), and molar refractivities (38) all show very small deviations from ideality.

The surface tension isotherms for the systems $\text{AgNO}_3\text{-NaNO}_3$ and $\text{AgNO}_3\text{-KNO}_3$ (Figures 7 and 8) show negative deviations from ideality. This deviation is obviously greater for the former system. The fact that the transport numbers of the ions in $\text{AgNO}_3\text{-NaNO}_3$ mixtures are proportional to their mole fractions (17), strongly supports the contention that there is complete dissociation in this system. The additivity of molar volumes (38, 42) and the small negative deviations from additivity of conductivity (42, 48) and molar refractivity (38) in $\text{AgNO}_3\text{-NaNO}_3$ and $\text{AgNO}_3\text{-KNO}_3$ mixtures all substantiate the idea that little or no ionic association takes place in these melts.

Surface tension isotherms in the system NaCl-KCl (Figure 9) show small negative deviations from ideality. This substantiates other physical measurements which have been made on this system (39). The shape of the surface tension isotherms is considerably different from those obtained by Barzakovskii (13); smooth curves cannot be drawn through his data.

If one compares the surface tensions of binary mixtures of salts with a common anion, the data suggest that deviations from ideality increase as the difference in size of the replacing cations increase. Boardman, Palmer, and Heymann (16)

and Semenchenko and Shikhobalova (12) also noted this trend in their surface tension data on binary mixtures. However, no conclusive statement can be made on the basis of the limited experimental data available.

Surface tension isotherms for the PbCl_2 -alkali metal chloride systems are shown in Figures 10-14. It is particularly interesting to note the minima in surface tension near 50 mole % in the PbCl_2 -KCl, PbCl_2 -RbCl, and PbCl_2 -CsCl melts. Such minima are not possible unless complex ions or some other surface active species are present in the melts at this concentration. If these melts were strictly two component systems, the presence of such minima in the surface tension isotherms would be a direct violation of the Gibbs absorption equation.

Evidence for complex ions in PbCl_2 -KCl and CdCl_2 -KCl melts is quite strong. Bloom and Heymann (20) explained the minima in equivalent conductivity in these mixtures in terms of anionic complexes. Activation energies for ionic migration and molar volumes show maxima at compositions corresponding to the minima in equivalent conductivity. The activation energies at certain compositions rise to very high values near the melting point of these salts indicating a high degree of order in these melts. It should be pointed out that it is dangerous to explain all conductivity minima in terms of complex ion formation unless there is a considerable amount of substantiating

evidence, since minima in equivalent conductivity have been observed in the systems LiCl-KCl (39) and $\text{CaCl}_2\text{-KCl}$ (49) in which the formation of complex ions is quite unlikely. Although transference studies on the system $\text{PbCl}_2\text{-KCl}$ now under way in this laboratory (21) give no direct evidence for the presence of an anionic complex, the ionic mobility-composition isotherms can most easily be explained by assuming some kind of aggregation or complexing in the melt. This complexing seems to have its maximum effect at a composition corresponding to the empirical formula $2\text{KCl}\cdot\text{PbCl}_2$. It is interesting that this compound has been shown to exist in the solid state (50).

The 575°C surface tension isotherms for the various PbCl_2 -alkali metal chloride systems are shown together in Figure 15 for convenience in comparing the change in the character of the isotherms as the size of the alkali metal cation in the melt increases. The isotherms for the system $\text{PbCl}_2\text{-LiCl}$ are practically linear over the composition range studied; the $\text{PbCl}_2\text{-NaCl}$ system exhibits small negative deviations from ideality; no minima were observed in these systems over the concentration range that was amenable to measurement. The exact location of the minima in the systems $\text{PbCl}_2\text{-KCl}$, $\text{PbCl}_2\text{-RbCl}$, and $\text{PbCl}_2\text{-CsCl}$ is difficult to determine, but minima most assuredly do exist in these isotherms whereas none were observed for the first two systems. The minima in the

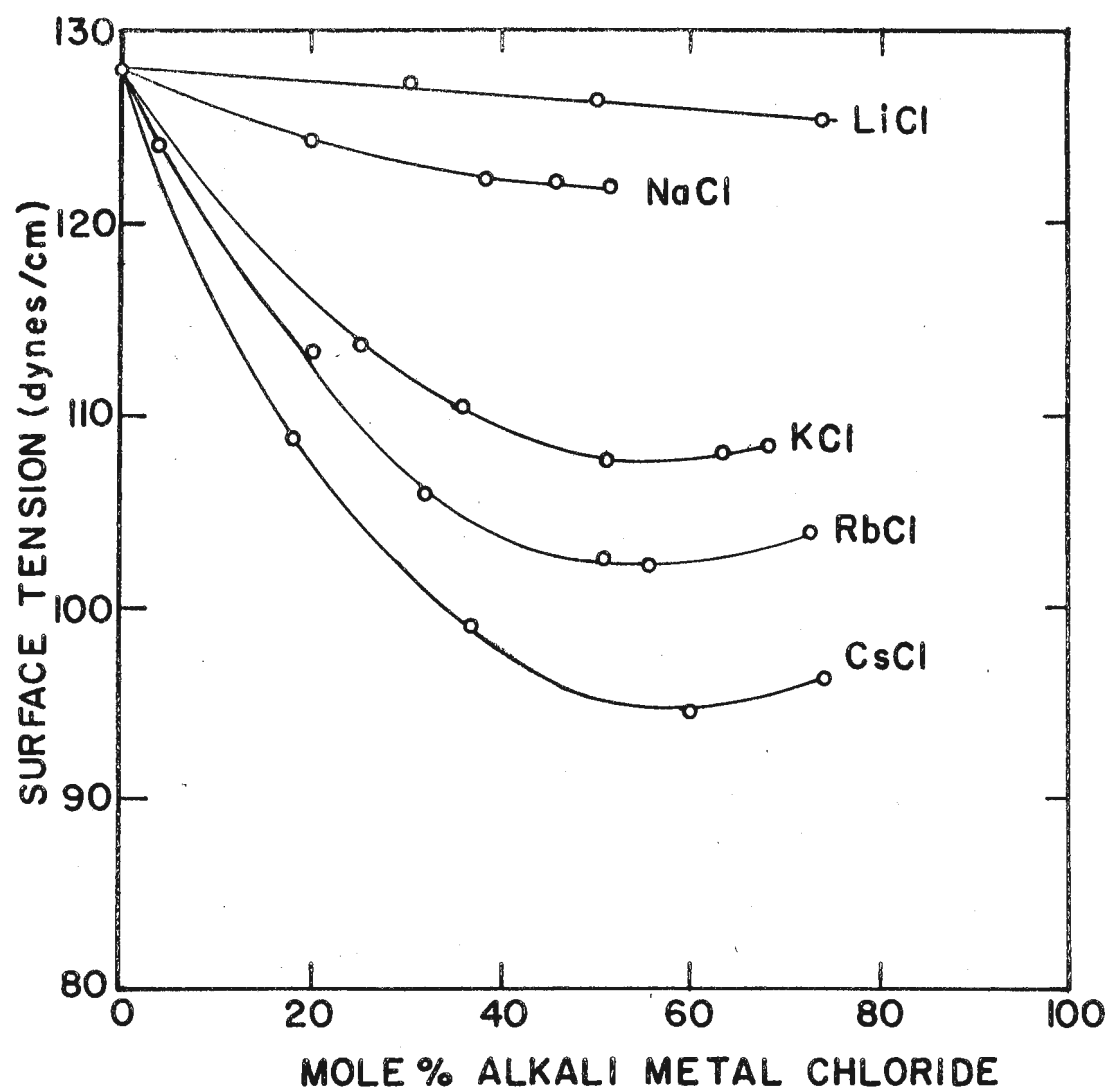


Figure 15. The 575°C surface tension isotherms in the PbCl_2 -alkali chloride systems

latter three systems appear to shift to higher mole % alkali chloride as the size of the alkali metal increases.

Similar trends were observed in conductivity isotherms for the systems $\text{CdCl}_2\text{-LiCl}$ (51), $\text{CdCl}_2\text{-NaCl}$ (20), and $\text{CdCl}_2\text{-KCl}$ (20). Whereas only small negative deviations from additivity were observed in the system $\text{CdCl}_2\text{-LiCl}$, somewhat larger negative deviations were found in the $\text{CdCl}_2\text{-NaCl}$ isotherms, and distinct minima were observed in the $\text{CdCl}_2\text{-KCl}$ system as was previously pointed out.

These experimental observations are in accord with the well-known fact that a smaller alkali metal ion has a greater polarizing power than a larger ion. Thus one would expect any anionic complexes in the melt to be more stable in the presence of a large cation with low polarizing power. This same qualitative effect of increased stabilization of certain anionic complexes by a larger cation is observed in the crystalline state. An X-ray investigation of $\text{Q}_4\text{AsFeCl}_4$ (52) showed the existence of discrete tetrahedral FeCl_4^{-1} ions. This complex anion is not known in the presence of smaller cations. X-Ray studies of the polyiodide complexes such as $\text{N}(\text{CH}_3)_4\text{I}_5$ (53) and $\text{N}(\text{CH}_3)_4\text{I}_9$ (54) also support this assumption. The resonance forms of the I_5^- and I_9^- ions are apparently stabilized by the large cations, since these ions have not been isolated with small cations. Hach and Rundle (53) suggested that as the cation in a polyiodide is made smaller, thus concentrating the

positive charge, the resonating form with the negative charge closest to the positive charge will be dominant and the resonance stabilization will decrease.

In addition to the trends in the character of the surface tension isotherms of the PbCl_2 -alkali metal chloride systems, interesting color changes were also observed in these melts. All the pure chlorides melt to colorless liquids with the exception of lead chloride which possesses a very faint yellow color. Mixtures of lead chloride with sodium chloride and lithium chloride are also colorless. However, there is a definite yellow color in the mixtures of lead chloride with potassium chloride, and the intensity of this color increases with an increase in size of the alkali metal ion in the melt. The PbCl_2 - CsCl mixtures are a beautiful canary yellow color; this color persists in the solid, but near room temperature the yellow disappears.

Although no unambiguous predictions concerning the nature of liquid mixtures can be made from a study of the phase diagrams, it is also interesting to note trends here. The phase diagrams for the systems PbCl_2 - LiCl (55) and PbCl_2 - NaCl (55) show simple eutectics, the system PbCl_2 - KCl (50) has one congruent melting point, the system PbCl_2 - RbCl (55) two congruent melting points, and the system PbCl_2 - CsCl (56) a very pronounced congruent melting point at 50 mole %. Caution must be used in predicting the existence of complex ions in the fused

state solely on the basis of congruently and incongruently melting solid state compounds indicated by phase diagrams.

The interpretation of various physical data on molten salts and their mixtures has provoked considerable interest concerning their structural nature. A number of investigators have explained their data on certain melts in terms of the existence of finite complex ions. Many have gone so far as to specify such finite ionic complexes as CdCl_3^- (20), CdCl_6^- (20), or CdCl_4^- (49) in the case of CdCl_2 -KCl melts, while for the PbCl_2 -KCl system the species Pb_2Cl_5^- (57), PbCl_4^{-2} (57), PbCl_6^{-4} (20, 57), and PbCl_3^- (20) have been predicted. The postulation of such species is based on the existence of their counterparts in aqueous solution which one must remember are also solvated or on the empirical formulas of the congruently and incongruently melting compounds indicated by the phase diagrams without regard to the actual structure of the complex.

In an effort to learn more about the nature of the anionic complexing in the PbCl_2 -alkali metal chloride melts a structural investigation of CsPbCl_3 by X-ray diffraction was undertaken (58). A 50% PbCl_2 -CsCl melt was allowed to cool slowly over a period of twenty-four hours. The isolated CsPbCl_3 crystals were found to be pseudo-cubic with a distorted perovskite structure similar to CsCdCl_3 (59). In this structure the cesium ions are at the corners of a cube, the lead

ions occupy the center of the unit cell, and chloride ions are approximately located on the centers of the faces. All the crystals examined showed a domain-type disorder, so no detailed structural analysis was carried out.

Three-dimensional lattice and chain-like structures of cadmium halide complexes with alkali cations also exist in the solid state; the cadmium ions always possess an octahedral coordination of chloride ions.

In the PbCl_2 -alkali metal chloride melts and similarly in the CdCl_2 -alkali metal chloride melts it then would appear reasonable to assume that the anionic complexing, stabilized by large cations such as K^+ , Rb^+ , or Cs^+ , consists not only of discrete ions postulated by other authors but of local aggregations of ions whose structures resemble the structure of the solid state. This increased local association in the melt must be such as to result in a low surface tension; the anionic complex must be more surface active than the other ions. It should be noted that the types of interionic forces involved in these systems are much different than those found in molten glasses since low rather than high surface tensions result from the association.

Evaluation of the Maximum Bubble Pressure Method

Although the maximum bubble pressure method is an excellent one to use in measuring the surface tensions of molten salts, some experimental difficulties do arise in work on viscous or highly volatile liquids.

Bubble formation in viscous liquids is frequently quite peculiar. Sometimes a very large bubble is produced which bursts into a number of small bubbles with a resultant step-wise pressure drop in the system; at other times the bubble does not burst despite a rise and fall of the pressure, or the pressure drop when the bubble bursts may be extremely slow and also abnormally small. Bubbles formed under the latter conditions can most aptly be described as "lazy" bubbles in contrast to "normal" bubbles with which there is associated a very rapid pressure drop in the system. Reproducible maximum bubble pressures can rarely be obtained when there is peculiar bubble formation.

Jaeger (8, 9) claimed success in measuring the surface tensions of viscous liquids by the maximum bubble pressure method. Parmelee and Lyon (60) were quite successful in applying it to molten glasses, although the technique they used to determine the maximum bubble pressures was somewhat different from that used in this work. The capillary tip was fixed at the surface of the melt; the pressure in the system

was allowed to increase until the bubble which formed had burst as indicated by a sudden drop in the pressure. The pressure was slowly decreased until a pressure was found which could be maintained for several minutes. This pressure was such that any observable increase resulted in the bursting of the bubble. This pressure was held constant for several minutes so there was ample time to read the upper and lower arms of the manometer. The author used their technique on non-viscous melts and found the maximum pressures to be identical with those measured at a bubble formation rate of one bubble per minute. Difficulties were experienced in getting pressures to remain constant when bubbles were formed in viscous liquids; sometimes the pressure kept rising to fantastically high values. Okhotin and Bazhbeuk-Melikova (61) found in their study of molten glasses that the surface tensions measured by the maximum bubble pressure method were some 50% higher than those obtained by other methods. Their difficulties were undoubtedly due to poor technique, since reliable results can be obtained with viscous liquids if the bubbles are formed very slowly. As was pointed out in the "Procedure" the reliability of a particular measurement can be estimated simply from the peculiar motion of the manometer liquid. The manometer height differences should be exactly reproducible if the system is at equilibrium.

Highly volatile liquids also present difficulties. In these cases the pressure changes in the system are indicative of "normal" bubble formation and yet one out of every four or five bubbles will show abnormally high pressures. Accurate results can be obtained only if care is used and the measurements are repeated a sufficient number of times. The high volatility of molten lead chloride made it virtually impossible to measure the surface tension of it or its mixtures above 625° C.

Peculiar bubble formation was observed at times with AgNO_3 and more frequently with PbCl_2 . This is the reason for the lesser degree of reproducibility found in the surface tensions of these melts. This peculiar bubble formation is not surprising, since the viscosities of these liquids are some three times greater than those of the alkali metal chlorides or nitrates. Measurement of the surface tension of ZnCl_2 was very difficult, since shortly after fusion the melt took on the color and consistency of maple syrup.

Analysis of Errors

The differential method will be used to calculate the maximum error. Surface tension was calculated from the relationship

$$\gamma = \frac{rg}{2}(hd_1 - id_2) - 1/3 d_2 r^2 g$$

where γ is the surface tension, g is the acceleration due to gravity, h is the manometer height difference in cm of dibutyl phthalate, d_1 is the density of the dibutyl phthalate, i is the depth of immersion of the capillary, and d_2 is the density of the melt.

The maximum error in γ is given by

$$\Delta\gamma = \frac{\partial\gamma}{\partial r}\Delta r + \frac{\partial\gamma}{\partial h}\Delta h + \frac{\partial\gamma}{\partial d_1}\Delta d_1 + \frac{\partial\gamma}{\partial i}\Delta i + \frac{\partial\gamma}{\partial d_2}\Delta d_2.$$

A consistent set of values for a typical surface tension measurement together with the maximum probable errors in each of the measured quantities are given below. These represent the data for a measurement on a NaNO_3 melt at 399°C .

$$r = 0.03254 \text{ cm at } 25^\circ \text{C}$$

$$r = \pm 0.0003 \text{ cm}$$

$$h = 7.265 \text{ cm}$$

$$h = \pm 0.006 \text{ cm}$$

$$d_1 = 1.0405 \text{ gm/cm}^3$$

$$d_1 = \pm 0.0002 \text{ gm/cm}^3$$

$$i = 0.2 \text{ cm}$$

$$i = \pm 0.001 \text{ cm}$$

$$d_2 = 1.845 \text{ gm/cm}^3$$

$$d_2 = \pm 0.002 \text{ cm}$$

$$g = 980.26 \text{ cm/sec}^2$$

$$\gamma = 114.5 \text{ dynes/cm}$$

Substitution of the appropriate quantities in the previous equation gives $\Delta\gamma = \pm 1.20 \text{ dynes/cm}$; the maximum relative error, $\Delta\gamma/\gamma$, is thus equal to ± 0.01 .

The most important contribution to $\Delta\gamma$ arises from the error associated with measurement of the capillary radius; in the particular example cited above the other errors together contribute less than ± 0.3 dynes/cm to $\Delta\gamma$.

The maximum relative error in surface tension is probably less than the ± 0.01 calculated above, since the capillary bore was reworked and remeasured if the measured surface tension of benzene did not agree within $\pm 0.5\%$ with the accepted literature value.

The temperature was measured to $\pm 0.5^\circ$ C; the maximum error is felt to be $\pm 1^\circ$ C. The importance of this error in temperature will depend on the magnitude of the temperature coefficient of surface tension. The temperature coefficients of surface tension range from 0.06 dynes/cm deg C for pure NaNO_3 to 0.1 dynes/cm deg C for pure PbCl_2 . Therefore the maximum probable error in reported surface tension due to error in temperature measurement will vary from ± 0.06 dynes/cm to ± 0.1 dynes/cm.

There is an additional error in the surface tensions of mixtures due to uncertainties in composition. This effect will be greatest in those regions in which the surface tension shows the greatest variation with composition. Assume that the analyses have a maximum probable error of ± 0.2 mole %. The greatest variation of surface tension with composition occurs in PbCl_2 -alkali metal chloride melts at high mole %

PbCl_2 where a 1% change in composition causes a change of 1 dyne/cm in the surface tension. This will result in a maximum probable error in γ of ± 0.2 dynes/cm. In the flat portions of these surface tension isotherms the error in surface tension due to error in composition will be zero.

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